PB-230 894

EMISSION FACTORS FOR TRACE SUBSTANCES

ENVIRONMENTAL PROTECTION AGENCY

DECEMBER 1973

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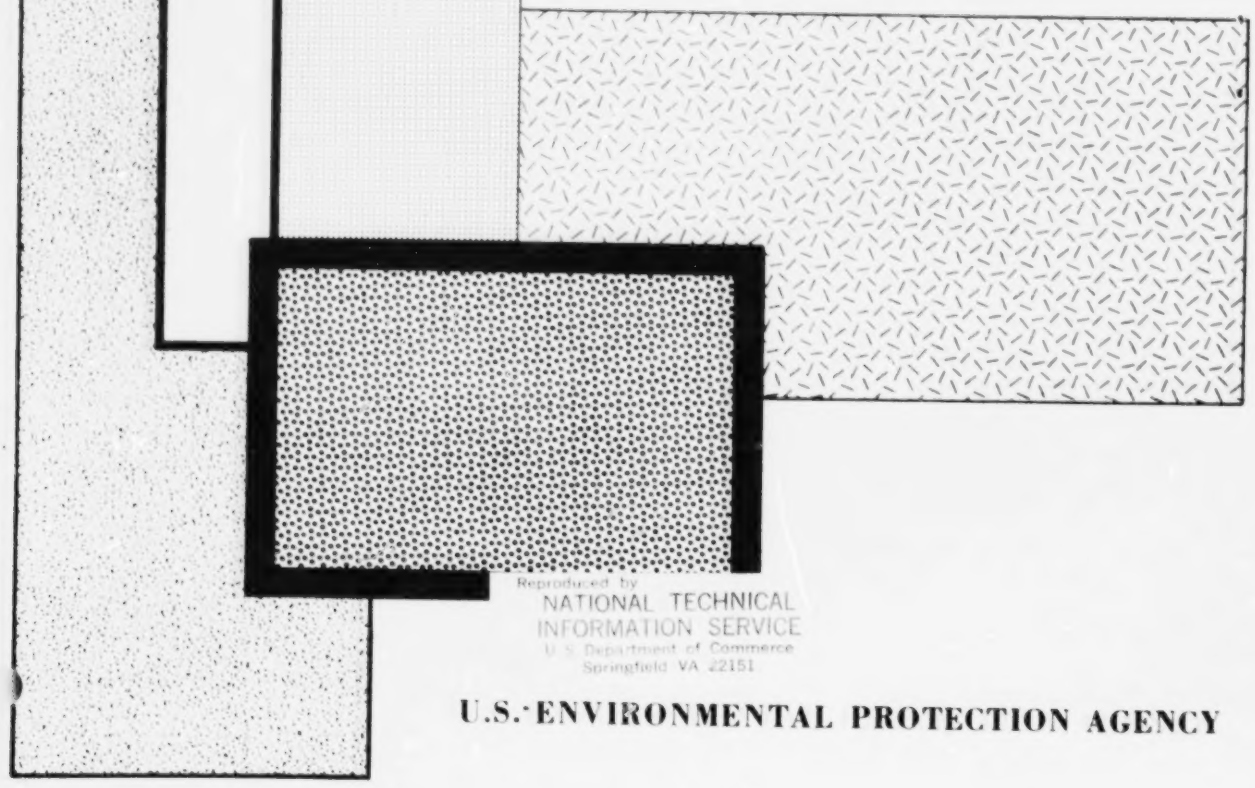

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BIBLIOGRAPHIC DATA SHEET	1. Report No. EPA-450/2-73-001	2.	3. Recipient's Accession No. PB-230 894
4. Title and Subtitle Emission Factors for Trace Substances			5. Report Date December 1973 6.
7. Author(s) David Anderson			8. Performing Organization Rept. No.
9. Performing Organization Name and Address U. S. Environmental Protection Agency Office of Air and Water Programs Office of Air Quality Planning and Standards Research Traingle Park, N. C. 27711			10. Project/Task/Work Unit No. 11. Contract/Grant No.
12. Sponsoring Organization Name and Address			13. Type of Report & Period Covered Final report 14.

15. Supplementary Notes

16. Abstracts

This document presents emission factors for eight trace pollutants: arsenic, asbestos, beryllium, cadmium, manganese, mercury, nickel, and vanadium. Emission data on which these factors are based, obtained from source tests, material balance studies, engineering estimates, etc., have been compiled for use by individuals and groups responsible for conducting air pollution inventories. Emission factors given in this document cover most of the common emission categories for the eight trace substances: mining, metallurgical, secondary metal industry, processing and utilization, consumptive uses, fuel combustion, and waste incineration. When no source test data are available, these factors can be used to estimate the quantities of the trace pollutants being released from a source or source group.

17. Key Words and Document Analysis. 17a. Descriptors

Air pollution *
Arsenic*+
Asbestos*+
Beryllium*+
Cadmium*+
Emissions+
Emission factors+
Manganese*+
Mercury*+
Nickel*+
Pollution*+
Vanadium*+

17b. Identifiers/Open-Ended Terms

*Emission factors
+Air pollution

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17c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
Release unlimited	UNCLASSIFIED	80
	20. Security Class (This Page) UNCLASSIFIED	22. Price 4.00

EPA-450/2-73-001

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by
David Anderson

1-9

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Water Programs
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711
December 1973

This report has been reviewed by the Office of Air Quality Planning and Standards, Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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PREFACE

This document presents emission factors that can be used to estimate emissions of eight trace substances: arsenic, asbestos, beryllium, cadmium, manganese, mercury, nickel, and vanadium. The limitations and applicability of emission factors, as presented in the Introduction to this report, should be kept in mind in applying the factors presented.

Throughout the document, some source classifications or industrial categories appear much more frequently than others. This is not intended to imply that these sources are necessarily more serious polluters than others. The imbalance is partially due to the availability of data from some more minor sources and the unavailability of equivalent data from other more obvious or more serious sources. When source tests are run, the emissions are normally analyzed for a wide range of constituents by the Environmental Protection Agency. Data from such analyses should aid considerably in the assessment of the relative importance of sources of a particular pollutant.

As additional data become available, they will be incorporated in this document as supplements. The availability of these supplements will be indicated in the publication, Air Pollution Technical Publications of the Environmental Protection Agency, which is available from the Air Pollution Technical Information Center, Research Triangle Park, N. C. 27711.

ACKNOWLEDGMENTS

The author would like to thank the people of the Environmental Protection Agency who have provided helpful suggestions and comments in preparing this document. These people are: James H. Southerland, John McGinnity, Mike Jones, Robert E. Neligan, John Copeland, Dr. Robert E. Lee, Darryl Van Lehmden, Dale Slaughter, Gill Wood, D. E. Caldwell, and Susan Anna. Susan Watson, Joan Currin, Vivian Dailey, Fannie Lee, and Cynthia Pendergrass were also very helpful in the production of the draft report.

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ABSTRACT

This document presents emission factors for eight trace pollutants: arsenic, abestos, beryllium, cadmium, manganese, mercury, nickel, and vanadium. Emission data on which these factors are based, obtained from source tests, material balance studies, engineering estimates, etc., have been compiled for use by individuals and groups responsible for conducting air pollution inventories. Emission factors given in this document cover most of the common emission categories for the eight trace substances: mining, metallurgical, secondary metal industry, processing and utilization, consumptive uses, fuel combustion, and waste incineration. When no source test data are available, these factors can be used to estimate the quantities of the trace pollutants being released from a source or source group.

Key words: air pollution, arsenic, asbestos, beryllium, cadmium, emissions, emission factors, manganese, mercury, nickel, pollution, vanadium.

EMISSION FACTORS FOR TRACE SUBSTANCES

1. INTRODUCTION

The purpose of this document is to present emission factors that can be used to estimate emissions of eight trace substances: arsenic, asbestos, beryllium, cadmium, manganese, mercury, nickel, and vanadium. It would be difficult and extremely costly to monitor suspect sources of large amounts of trace substances within the United States. The only feasible method of determining trace substance emissions for a given community is to make generalized estimates of typical emissions from each of the source types.

The emission factor is an estimated average of the rate at which a pollutant is released to the atmosphere as a result of some activity, such as combustion or industrial production, divided by the level of that activity.[1]

The limitations and applicability of emission factors must be understood. While the emission factors presented in this report are sufficient, under most conditions, for estimating emissions for such purposes as emission inventories, their accuracy is uncertain and in most cases unknown. They should not be used as a basis for establishing control regulations, standards, or similar measures. In general, particle size distribution and chemical structure were not considered in developing the factors because of the lack of such data.

The emission factors presented in this document were estimated by the whole spectrum of techniques available for determining such factors; these included: questionnaire surveys, plant visits, source testing, process material balances, analytical work to determine the content of trace substances, and literature search. Obviously, the varying accuracies of the techniques employed in developing the emission factors affect the accuracy of the emission factors themselves. To give some indication of this variation, the tables include an "emission factor symbol" that indicates the technique employed to determine each emission factor. Emission factor symbols commonly used in this document are defined in Table 1-1[2-16] and the accuracy normally associated with the related techniques is indicated. In some instances, analytical techniques not included in Table 1-1 were used to determine emission factors for a specific trace substance or the accuracy of the technique differed for a specific substance from that given in Table 1-1. These exceptions are identified in the introduction to the chapter pertaining to the particular substance involved.

In using these factors, the following procedure is recommended. First, the user should read Table 1-1. Next, the text description of the emission source should be read. Finally, based on this information, the factor can be intelligently applied to the area of concern.

Unless otherwise noted in the tables, the emission factors are for uncontrolled processes. In some cases, however, it was impossible to develop uncontrolled factors, and in these instances, factors were developed based on emissions from control equipment. No attempt should be made to back calculate to obtain the uncontrolled value since this could lead to large errors and possibly to undue concern. Therefore, factors of this type should only be applied to controlled processes.

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Table 1-1. EMISSION FACTOR SYMBOLS

Emission factor symbol	Technique	Estimated accuracy
PV	Plant visits	Unknown.
E	Engineering judgement	Unknown.
Q	Questionnaire surveys	Unknown.
MB	Material balances	Unknown.
Source sampling		
CAA	Flame atomic absorption	Precision is 1, 3, and 10% for minimum detectable levels of 1, 0.5, and 0.1 ppm, respectively, for beryllium and for nickel in oil samples.[2] Minimum detectable level is 0.4 ppm for cadium in oil samples.[2] Minimum detection limit is 0.001 μg/ml of prepared sample for cadmium generally.[3] Less accurate than FAA for mercury.[4]
DM	Dithizone	Comparable to FAA for mercury analysis.[5]
ES	Emission spectroscopy	Semiquantitative.[6]
EST	Emission spectrometry	Semiquantitative.[7]
FAA	Flameless atomic absorption	±5% with minimum resolution of 2 ppb for analysis of mercury.[8,9]
NA	Neutron activation	± 25% for one sample of particulate analyzed.[11] Arsenic in biological materials had an average deviation of about ±6.9%.[12] ± 20% precision for mercury in coal.[13] Accuracy of ±5% for biological tissues analyzed for cadmium.[14]
OES	Optical emission spectrography	Considered to be semiquantitative. Reported to have a precision of ± 25% for samples from cement plants.[10]
S	Saltzman's colorimetric	Unknown.[15]
SC	Spectrochemical analyses	Limit of detection is 0.0001% with an accuracy of ± 15% for beryllium analysis in coal.[16]
SSMS	Spark source mass spectrography	Precision ± 100%.[10]
UK	Unknown, reported in literature based on unspecified analytical technique	Unknown.

2. ARSENIC

MINING[1]

Arsenic is widely distributed in the earth's crust. It occurs mainly as an impurity in copper, lead, cobalt, nickel, iron, gold, and silver ores. Emission of arsenic is a by-product of mining for these ores.

Processing is basically the same for all mining operations: ore removal, ore handling, crushing, grinding, and concentration. Emissions of arsenic occur from these operations, but the major part is from tailings (wind losses). The emission factor for mining operations is given in Table 2-1.

METALLURGICAL PROCESSING[1]

Arsenic is produced commercially from flue dust, speiss, and sludges as a by-product of copper smelting and other smelting operations. It is produced in the form of arsenic trioxide or arsenous oxide (As_2O_3). The arsenic trioxide is volatilized during smelting and is, therefore, a main constituent of flue dust. Crude flue dust can carry up to 30 percent by weight of arsenic trioxide.

To recover arsenic trioxide from the flue dust (or from the other sources mentioned), the crude flue dust is mixed with a small amount of pyrite or galena. The hot gases from the roasting (about 220°C) are passed through brick cooling chambers called kitchens (about 100°C). Arsenic trioxide will condense out of the gas as a result of cooling, and the condensate is 90 to 95 percent pure arsenic trioxide.

If higher purity is necessary, the arsenic trioxide is refined in a reverberatory furnace (at 540 °C). The vapors pass through settling chambers and kitchens. The temperature (from 120 to 180 °C) in the settling chambers is above the condensation point of the trioxide. Most of the trioxide is thus caught in the kitchens and is about 95 percent pure. A baghouse is used for exit gases from the kitchens.

Emissions occur as a result of gas losses during processing. Some dust is also lost. In processes in which arsenic content of the ore is high, control equipment is an essential part of the process. Other smelters dump the flue dust or sell it to refining smelters.

Emission factors are provided in Table 2-1 for copper, lead, and zinc smelters. No emission factors are provided for gold and silver reduction plants. These values can be considered uncontrolled emissions since the arsenic is usually collected as flue dust. The emission factors are based upon material balances and stack sampling data.

CAST IRON[1]

Dust samples from foundries have been analyzed by spectrographic methods for arsenic content. Foundries and steel mills emit arsenic, the quantity depending upon the content of the raw materials.

The cupola is used most extensively in the production of cast iron. Based on information obtained from the industry, the particulate emission factor is 9 to 11 kilograms of particulate per 1000 kilograms of process weight. This value includes melting and nonmelting operations. Arsenic constitutes about 0.7 percent of this particulate matter.[1] Therefore, from the above information, the emission factor for this industry was estimated as shown in Table 2-1.

NONFERROUS ALLOYS[1]

Arsenic is alloyed with copper (arsenical copper), lead, and sometimes brass. Arsenical copper can contain from 0.3 to 0.5 percent arsenic. Certain lead alloys contain from about 1 to 2.5 percent arsenic.

Uses for arsenical copper are for building automobile radiators, heat exchangers, and condenser tubes. Batteries, babbits, and munitions use lead containing a small quantity of arsenic. Arsenic is also added to small quantities of brass to prevent dezincification and reduce season cracking.

Alloying and melting operations for the production of these alloys result in emissions, and no air pollution equipment is reported in use. The

emission factor (Table 2-1), based on information obtained from industry, is therefore, considered an uncontrolled value.

PHOSPHORIC ACID, THERMAL PROCESS [1]

Some phosphoric acid produced by the thermal process is used in detergents, foods, and drugs. Phosphates used to produce the phosphoric acid will, from natural sources, contain arsenic. The phosphates are reduced in an electric furnace, and during this step, arsenic emissions may be quite significant. However, no emission factor is available to date.

PROCESSING AND UTILIZING ARSENIC AND ITS COMPOUNDS [1]

About 70 percent of the arsenic and its compounds consumed is for agricultural purposes, 20 percent is used in glass production, and the rest (about 10 percent) goes for wood preservatives, nonferrous alloys, animal dips, paints, pyrotechnics, poultry feeds, and other products. Emission factors are provided in Table 2-2.

Agricultural Uses [1]

The principal use of arsenic is in the application of various arsenic compounds as pesticides. All compounds are produced from arsenic trioxide.

The processing of the pesticides depends upon the size of operation. Small operations conduct all reactions in closed batch reactors. Emissions occur only as handling losses before the arsenic trioxide is added to the reactor vessel. In large operations, arsenic trioxide is handled in bulk quantities. In some cases, for example, trioxide is received in railroad cars and dumped directly into a reactor tank containing nitric acid to produce arsenic acid. The chemical reactions involving the trioxide with various other reactants do not result in significant emissions. Most handling operations are controlled by hoods, ducts, exhaust fans, and baghouses.

The emission factor presented in Table 2-2 is based on information obtained from industrial sources. The value is considered a controlled emission factor.

Glass Production [1]

Arsenic is used in almost all types of glass. It aids the processing by removing bubbles during manufacturing and acts as a stabilizer of selenium in decolorizing crystal glass. About 1 to 5 kilograms of arsenic per 1000 kilograms of glass produced is used. Soda-lime glass, the most widely used glass, will contain about 3 kilograms of arsenic per 1000 kilograms of glass.

The process normally involves a direct-fired regenerative furnace that operates continuously. Raw materials are charged at one end of the furnace and molten glass exits at the other end. The operating temperature inside the furnace is about 1480°C, and the exit temperature of the glass is about 1200°C. Emissions are mainly from the furnace as combustion gases, and volatilized materials from the molten mass. The mass of particulates emitted is directly proportional to the production rate of the furnace.

No stack information or material balance information is available to yield emission factors. However, 7.71 percent of the particulate emitted (about 1 kilogram per 1000 kilograms of glass) has been reported to contain arsenic trioxide. The emission factor based on this information is presented in Table 2-2. Samples from baghouses yielded this value; however, the value 7.71 percent is considered an uncontrolled emission, and the emission factor given should be used for uncontrolled processes only.

Wood Preservatives [1]

Several arsenic compounds are used as wood preservatives. These compounds are used to preserve mine timbers, telephone poles, and other wood materials. Emissions from this source are considered negligible.

Others [1]

Other uses of arsenic and its compounds are represented in paint pigments, pyrotechnics, cattle and sheep dips, pharmaceuticals, poultry feed additives, semiconductors (alloyed with aluminum, gallium, and indium), and other miscellaneous products.

Industrial sources felt that emissions from these applications in industry resulted from handling of the dry arsenic or its compounds. The emission factor is based on information from these sources and should be used for the individual industries (see Table 2-2).

CONSUMPTIVE USES

Agricultural [1]

The uses of spray and dust pesticides containing arsenic and its compounds are sources of emissions as a result of application (consumptive use). No emission factor is available at present on spraying or dusting operations because of lack of data.

Another source of emissions from spraying or dusting operations is from cotton ginning operations. Here pesticides adhere to cotton fibers, and emissions result from the ginning operation. In one study, particulates from a cotton gin were taken. Particulate discharge was determined to be about 5.9 kilograms per bale of cotton ginned. The arsenic content of the particulates average about 0.03 percent. Using the amount of particulate emitted and the percent of arsenic present, the emission factor was estimated (Table 2-3).

Detergents [1]

Arsenic is not added to detergents intentionally. The arsenic occurs naturally in the phosphates used in producing detergents. Emissions are considered negligible.

FUEL COMBUSTION

Coal [1,2]

The average content of arsenic in domestic coal is about 5.44 parts per million. During combustion, arsenic is emitted with the fly ash. A study of fly ash samples showed an arsenic range of 25 to 370 micrograms per cubic meter (by emission spectrographs).[2] Based on an average value (147 micrograms per cubic meter) obtained from the fly ash samples taken from stacks, the emission factor (sample taken after fly ash collection) was calculated (Table 2-4).

Oil [3]

Imported fuel and crude oils and United States crude oils have been analyzed by neutron activation. All but one sample of the imported residual oils analyzed contained arsenic. The arsenic content of the residual oils ranged from 0.1 to 0.2 part per million with an average of 0.14 part per million. All foreign crude oils analyzed showed arsenic to be present. The arsenic content of the crude oils ranged from 0.01 to 0.34 part per million with an average of 0.13 part per million. Only five out of nine U.S. crude oils analyzed showed arsenic to be present. The arsenic content of the U.S. crude oils ranged from 0.007 to 0.61 part per million with an average of 0.15 part per million.

The emission factors given in Table 2-4 are based on the arsenic content in the oils; a 100 percent combustion factor and densities of 850 (crude oil) and 944 grams per liter (fuel oil) were assumed.

WASTE INCINERATION [1]

Burning of products that contain arsenic is a waste incineration source. No overall emission factor for this source is available.

Two emission factor values are available: cotton ginning waste burning and sewage and sludge burning (Table 2-5). Waste from cotton ginning operations will contain arsenic as a result of pesticide application to cotton fields. The emission factor for cotton ginning was estimated by Davis.[1] For sewage and sludge, the arsenic content ranges from 2 to 3.4 parts per billion. Based on these values, the emission factor in Table 2-5 was estimated by Davis.[1]

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Table 2-1. EMISSION FACTORS FOR MINING AND INDUSTRIAL SOURCES OF ARSENIC

Source	Emission factor	Emission factor symbol[a]
Mining	0.1 kg/10^3kg (0.2 lb/ton) of arsenic in ore	E
Copper smelter	3 kg/10^3kg (5 lb/ton) of copper	MB, UK
Lead smelter	0.4 kg/10^3kg (0.8 lb/ton) of lead	MB, UK
Zinc smelter	0.5 kg/10^3kg (1 lb/ton) of zinc	MB, UK
Cast iron	0.006 to 0.008 kg/10^3kg (0.01 to 0.02 lb/ton) of metal charged	E
Nonferrous alloys	0.5 kg/10^3kg (1 lb/ton) of arsenic processed	Q

[a] Defined in Table 1-1.

Table 2-2. EMISSION FACTORS FOR PROCESSING ARSENIC AND ITS COMPOUNDS

Source	Emission factor	Emission factor symbol[a]
Pesticide production for agricultural uses[b]	10 kg/10^3kg (20 lb/ton) of arsenic processed	Q
Glass production	0.08 kg/10^3kg (0.2 lb/ton) of glass produced	OES (1)
Wood preservatives	Negligible	—
Others (paint pigments, pyrotechnics, pharmaceutical, semiconductors, etc.)	2 kg/10^3kg (3 lb/ton) of arsenic processed	Q

[a] Defined in Table 1-1; number in parentheses indicates the number of samples analyzed.

[b] Controlled emission factor.

Table 2-3. EMISSION FACTORS FOR CONSUMPTIVE USES OF ARSENIC

Source	Emission factor	Emission factor symbol[a]
Cotton ginning processing	2 kg/10^3 bales (4 lb/10^3 bales) of cotton ginned	UK
Detergents	Negligible	—

[a] Defined in Table 1-1.

Table 2-4. EMISSION FACTORS FOR ARSENIC FROM FUEL COMBUSTION

Fuel and source	Arsenic content, ppm	Emission factor		Emission factor symbol[a]
		kg/10^3 liters	lb/10^3 gallons	
Coal, domestic, controlled	5.44	2[b]	3[b]	OES (1)
Foreign residual oil				
No. 6 fuel oil, Mexico	0.1	0.00009	0.0008	NA (1)
No. 6 fuel oil, Virgin Islands	0.1 to 0.2	0.00009 to 0.0002	0.0008 to 0.002	NA (2)
No. 6 fuel oil, Trinidad	0.095	0.00009	0.0007	NA (1)
No. 6 fuel oil Curacao, N.A.	0.16 to 0.2	0.0002	0.001 to 0.002	NA (2)
Average for foreign residual oil	0.14	0.0001	0.001	NA (8)
Foreign crude oils				
Neutral zone crude No. 24	0.079	0.00007	0.0006	NA (1)
Boscan crude oil, Morovia	0.34	0.0003	0.002	NA (1)
Jabo crude oil, Venezuela	0.053	0.00005	0.0004	NA (1)
Kuwait crude oil, Kuwait	0.01	0.000009	0.00007	NA (1)
Boscan crude oil, Venezuela	0.31	0.0003	0.002	NA (2)
Lagunillas crude oil, Venezuela	0.12	0.0001	0.0009	NA (1)
UMM Farvo, Libya	0.02	0.00002	0.0001	NA (1)
Average for foreign crude oils	0.13	0.0001	0.0009	NA (8)
U.S. crude oils				
St. Tedesa, Illinois	0.61	0.0005	0.004	NA (1)
Maysville, W. Oklahoma	0.031	0.00003	0.0002	NA (1)
Hall-Gurney, Kansas	0.047	0.00004	0.0003	NA (1)
East Texas, Texas	0.007	0.000006	0.00005	NA (1)
Grass Creek, Walker Dome, Wyoming	0.04	0.00003	0.0003	NA (1)
Average for U.S. crude oils	0.15	0.0001	0.001	NA (5)

[a] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.

[b] Units for coal are kilograms per 10^3 kilograms and pounds per 10^3 tons, respectively.

Table 2-5. EMISSION FACTORS FOR ARSENIC FROM SOLID WASTE INCINERATION

Source	Emission factor	Emission factor symbol[a]
Cotton ginning waste burned	9 kg/10^3 bales (17 lb/10^3 bales) of cotton ginned	E
Sewage and sludge	0.01 kg/10^3kg (0.02 lb/ton) of sewage and sludge	E

[a] Defined in Table 1-1.

3. ASBESTOS

MINING [1,2,3]

Mineral abestos occurs in serpentine ore. The most economical form of abestos is in the fibrous form called chrysotile. The ore may contain up to 30 percent abestos, but the average is 4 percent.[2] The mining of abestos is normally open pit or underground. The process for open-pit operations consists of drilling, blasting, sorting and/or hand cobbing, shovelling, transportation, and dumping at the mill area. Underground operations involve mining in drifts and stopes, using modified room-and-pillar methods.[1,2,3]

Emissions are considered negligible for underground operations, but emissions result from all open-pit operations. Drilling operations are controlled by cyclones or by filter bag collecters, the latter being more effective. Controls for blasting consist of wetting the blast area and sizing the explosive charge. To reduce emissions from trucks carrying the ore, tarpaulins are sometimes employed. The emission factors presented in Table 3-1 were estimated by Davis[1] and Harwood.[2] Both controlled and uncontrolled emission factors are presented.

MILLING [1,2]

Abestos milling processes consist mainly of course crushing, drying, recrushing in stages, screening for stages, fiberizing, grading, and bagging. Emissions result from handling between each process step of crushing, drying screening, and bagging and from tailings. Completely enclosing an operation is the most widely used control technique. This technique is used for crushing, screening, fiberizing, and conveying. Exhaust hoods, cyclones or a combination of these are also used for all processes. A dumper unit or earth covers and plantings are sometimes used to reduce tailings emissions. The emission factors presented in Table 3-1 are based on estimates made by Davis[1] and Harwood.[2]

PROCESSING OF ASBESTOS

Friction Products [1,2]

Friction products, such as brake linings, consist of asbestos fabric or molded asbestos in a specific matrix. Processing consists of wet mixing, grinding, drilling, and trimming. Each process produces emissions, but because of the matrix formation, complete fibers will usually not be emitted. Emissions are controlled by capture hoods, ductwork, fans, and bag filters. The emission factor in Table 3-2 is based on a manufacturer's estimated loss of 0.25 to 0.50 percent of asbestos from a bag filter.[1,2]

Asbestos Cement Products [1,2]

Asbestos cement products contain from 15 to 20 percent by weight of asbestos. The largest use is in asbestos-cement pipes. Asbestos cement is also used in conduits for electric and telephone cables, roofing shingles, insulation boards, etc. The processing consists mainly of asbestos fibers being dry-mixed with ground silica and portland cement. Water is added to produce a slurry that is molded or wound on a rotating metal cylinder to form pipes. Shingles and siding products are sometimes manufactured by a dry process in which a dry mix is spread over a conveyor belt before water is added. In the wet process, water is added before forming. The last steps in all of the products are the finishing steps: sawing, turning, drilling, and sanding. Emissions result from handling, dry mixing, and finishing steps. Emissions from finishing steps are controlled by a complex ventilation system consisting of capture hoods, ductworks, fans, and filters. Wet and dry cyclones, baghouse filters, or a combination of these reduce emissions from mixing. The emission factor in Table 3-2 for this industry is based on Davis' estimate.[1]

Textiles [1,2]

Of the five varieties of commercial asbestos, only chrysotile, crocidolite, and amosite can be used in the textile industry. Asbestos is received by the textile mill in milled form, or sometimes in crude form. Crude asbestos is received in unopen bundles and is cleaned by edge mills. The output from the edge mills is screened, graded, and stored. The milled and newly separated fibers from crude asbestos are fed into "willowers" or "moody

fluffers," which fluff up the fibers.[2] Next the fibers are mixed with a small amount of cotton or other organic fiber just before the carding process. After carding, the fibers are placed on lap aprons to yield rovings. The rovings are spun into yarns, and the yarns are sometimes further processed to produce twine or cord.

Emissions result from the edge mills, willowing process, spinning and weaving of the yarns, and screening and conveying of the fibers. Air ventilation systems to baghouse filters are employed on almost all processes. For the spinning and weaving process, emissions can be quite significant. Emissions can be reduced by wetting fibers and by adding organic fibers. The uncontrolled emission factor in Table 3-2 was estimated by Harwood;[2] the controlled factor was estimated by Davis.[1]

Asbestos Paper [1,2]

Processing in the production of asbestos paper is similar to the processing of wood pulp to obtain paper.[1] Asbestos paper contains approximately 80 percent asbestos.[2] The other ingredients are china clay and sodium silicate or starch. The mixture is dried and mixed, then water is added to produce a slurry. The slurry is conveyed to a paper machine where sheets of paper are formed. The sheets are rolled and dried. The handling and mixing of dry products result in the various sources of emissions from this industry. Emissions are controlled by baghouses and cyclones. The uncontrolled emission factor in Table 3-2 was estimated by Harwood;[2] the controlled factor was estimated by Davis.[1]

Floor Tile [1,2]

In manufacturing floor tiles, asbestos fibers are bonded with polymers or copolymers of vinyl and/or vinylidene compounds. The processing consists of mixing, milling, calendering, water spraying, buffering, punch pressing, and packaging. The dust collected from each process is recycled to the crusher and then to the punch press. Emissions are collected for all processes by cyclones or bag filters.[1] The emission factors presented in Table 3-2 were estimated by Harwood.[2]

Asbestos Insulation [1]

A combination of calcium silicate with asbestos produces an effective insulator, which is usually employed on steam pipes. The process consists of mixing calcium silicate (85 percent) with asbestos and water. Not enough information is available to obtain an accurate emission factor.

Others

The manufacture of asbestos-asphalt products, paints using asbestos fibers, and some molded articles can also result in asbestos emissions. However, not enough information is available to estimate emission factors for these processes.

CONSUMPTIVE USES [1,2]

Emissions from the application of asbestos and products containing asbestos are caused by friction, cutting, handling, or spraying. The emissions result from asbestos-asphalt road surfacing, brake linings, insulation used in the construction industry, steel fireproofing (spray-on materials), and insulating cement. Emission factors for each (except road surfacing) are presented in Table 3-3. The emission factors for brake linings are based on a 0.5 percent loss of the 1.4 kilograms of asbestos in the lining. Steel fireproofing (mixture of asbestos, cement, and mineral wool) is done in an enclosed area in which it is assumed by Davis[1] that 75 percent of the emissions are controlled. Insulating cement is used extensively in all types of boilers. The emission factor presented in Table 3-3 is based on an assumed 89 percent control of 15 percent loss of abestos present in the cement.[1] The basis for the emission factor given for construction is unknown.[2]

SOLID WASTE INCINERATION [1]

Various products that contain asbestos are discarded, and the waste material may be incinerated. This alone could become a large emission source of asbestos; however, no accurate information is available to determine an emission factor.

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Table 3-1. EMISSION FACTORS FOR ASBESTOS FROM MINING AND MILLING[a]

Source[b]	Emission factor, kg/10^3kg (lb/ton) of asbestos produced	Emission factor symbol[c]
Mining, total	5 (9 to 10)	E
Mining	2 (3)	E
Loading	1 (2)	E
Hauling	1 (2)	E
Unloading	1 (2)	E
Mining, total, 50% control	3 (5)	E
Milling	50 (100)	E
Milling, 50% control	40 (80)	E
Milling, 80% control	10 (20)	E

[a]The emission factors are based on engineering estimates and no source sampling. These factors cannot be used to quantify asbestos emissions.

[b]Uncontrolled unless otherwise specified.

[c]Defined in Table 1-1.

Table 3-2 EMISSION FACTORS FOR PROCESSING OF ASBESTOS [a]

Source [b]	Emission factor, kg/10^3kg (lb/ton) of asbestos processed	Emission factor symbol [c]
Friction material, controlled	3 (6)	Q
Asbestos cement products, controlled	0.5 (1)	E
Textiles	20 (40)	E
Textiles, controlled	1 (2)	E
Asbestos paper	2 (4)	E
Asbestos paper, controlled	0.5 (1)	E
Floor tile	2 (4)	E
Floor tile, controlled	0.5 (1)	E

[a] The emission factors are based on engineering estimates and no source sampling. These factors cannot be used to quantify asbestos emissions.

[b] Uncontrolled unless otherwise specified.

[c] Defined in Table 1-1.

Table 3-3. EMISSION FACTORS FOR CONSUMPTIVE USES OF ASBESTOS [a]

Source [b]	Emission factor, kg/10^3kg (lb/ton) of asbestos applied	Emission factor symbol [c]
Brake linings	5 (10)[d]	E
Steel fireproofing, controlled	5 (10)	E
Insulating cement, controlled	13 (25)	E
Construction industry	13 (25)	E

[a] The emission factors are based on engineering estimates and no source sampling. These factors cannot be used to quantify asbestos emissions.

[b] Uncontrolled unless otherwise specified.

[c] Defined in Table 1-1.

[d] A factor of 0.0005 pound per 10^3 vehicle miles can also be used.

4. BERYLLIUM

MINING [1]

Beryllium is found in beryl, bertrandite, phenacite, chrysoberyl, and barylite ore. The main commercial source in the United States is beryl ore.

Processing consists of a cycle of drilling, blasting, cobbing, hauling waste to dumps, and concentrating by hand-sorting. Emissions can result from all of the processes mentioned. The emission factor in Table 4-1 is based upon Davis' estimation.[1] Emissions can also occur from copper mining operations, but no emission factor is available at present.

METALLURGICAL PROCESSING

Beryllium Hydroxide [1,2]

The basic product from beryl ore is beryllium hydroxide. Two processes are used for the production of beryllium hydroxide: the Copaux-Kawecki flouride process and the Sawyer-Kjillgren process. In the former process, the beryl ore is powdered by dry grinding, mixed with soda ash and sodium flousilicate, and sintered at 760°C. The product is then crushed, ground, and leached with water. The insolubles in the water are filtered, and the filtrate is treated with caustic soda to precipitate the beryllium hydroxide.

In the Sawyer-Kjillgren process, a sulfate extraction process, beryl ore is crushed, melted at about 1760°C, and quenched in water to destroy the crystaline structure. Next, the beryl glass is placed in a gas-fired rotary kiln at 930°C, ground in a ball mill to increase its activity, and then added to sulfuric acid and water. Then soluble beryllium and aluminum sulfate are extracted. Most of the aluminum is removed by the addition of ammonium hydroxide. The resulting solution is cooled, and the alum is separated by centrifuging. As the final steps for the production of beryllium hydroxide ore, chelating agents are added to the filtrate after centrifuging, sodium hydroxide is added to produce sodium beryllate, beryllium hydroxide is formed by hydrolysis, and the beryllium hydroxide is separated by centrifuging.

Emissions are controlled from existing plants using processes discussed. Ore storage, crushing, melting, quenching, heat treatment, grinding, and handling are all controlled by cyclones and baghouses. Sulfation and dissolving are controlled by a packed tower water scrubber. Crystallization and beryllation, and sometimes leaching, are controlled by ventilation. A venturi scrubber is used on filtration and sintering processes and sometimes leaching processes. No emission factor is available for the production of beryllium hydroxide.

Beryllium Oxide [1]

To produce beryllium oxide, beryllium hydroxide is redissolved in water and sulfuric acid, and ammonium sulfide is added to the solution. The solution is then filtrated, evaporated, and crystallized. Centrifuging is done to obtain beryllium sulfate, which is then blended and calcinated at 1040°C to yield beryllium oxide. Emissions are controlled by ventilating and by a packed tower caustic scrubber (for the blending and calcining step). No emission factor can be determined at present.

Beryllium-copper Alloys [1]

In the production of beryllium-copper alloys, a master alloy is first produced. The process involves beryllium hydroxide, which is calcined at 430°C to produce beryllium oxide. Known quantities of carbon powder, beryllium oxide, and copper are mixed, melted in an electric arc furnace, and then cast into ingots containing 4 percent beryllium. Finally, the ingots plus more copper are melted in an induction furnace to form 2 percent beryllium-copper alloys. Emissions from calcining, mixing, melting (induction furnace), and casting are all controlled by baghouses. Arc furnace emissions are controlled by a cyclone and baghouses. Not enough information is available to determine an emission factor.

Beryllium Metal [1,2]

Beryllium fluoride is used by the primary producers for the production of beryllium metal. One process used is the Schwenzfeir-Pomelee purification process. Here, the feed contains sulfate extraction product and various recycled products

that are used to produce beryllium fluoride. The feed is dissolved in ammonium bifluoride, calcium carbonate is then added, and the solution is thickened to remove heavy metals (except manganese and chromium). Lead dioxide is added to produce insoluble manganese dioxide and lead chromate, which are filtered out. Next, the mixture is sulfated, filtered again, placed in a vacuum crystallizer, centrifuged, dried, and placed in a decomposition furnace. Ammonium fluoride is volatilized, and beryllium fluoride is removed and solidified. An excess of beryllium fluoride is added to magnesium, and a slag with a melting point below the melting point of beryllium is produced. The excess is essential for beryllium metal to be obtained by water leaching. Solid beryllium is obtained by raising the temperature above the melting point of beryllium (1260°C). The mass is then poured into a receiving pot, solidified, crushed, and water-leached in a ball mill. To eliminate the impure magnesium, the metallic beryllium is melted again, and nonvolatiles are removed in a dross. Emissions from each individual process are controlled by a venturi scrubber, packed tower scrubber, hydraulic scrubber, baghouse, cyclone, or a combination of these control devices.[1,2]

No emission factor for the production of beryllium metal can accurately be determined. However, for the entire processing of beryllium metal, alloys, and compounds (which is usually done at one plant) an overall emission factor is provided in Table 4-1. The emission factor is based upon stack sampling information obtained by the Environmental Protection Agency (EPA).[1]

CEMENT PLANTS

Dry Process [3,4]

Beryllium is present naturally in the initial materials used to produce cement (pyrite, limestone, clay, and shale). In the dry process, limestone is crushed, then ground or ball milled (sometimes with clay). Shale and pyrite are added, and the product is pneumatically pumped into blending silos. After the silos, the material is fed to a kiln, then to a clinker cooler where gypsum (4.45 percent by weight) is added, and the product is fed to a finishing mill. After the mill, the material enters an air separator or classifier where the finished cement is pneumatically pumped to silos. Emissions from dry-process cement plants result from all of these processes.

Two plants using the dry processing method were visited, and particulate samples were obtained by the EPA sampling train method.[4] Baghouses at both plants were employed as air pollution control equipment. The probes for the sampling train were placed in the stack area after each baghouse. Some of the samples (total catch) were analyzed by emission spectroscopy for trace metals. The emission factors (Table 4-1) were calculated from the percent of beryllium present in the sample and the emission factor calculated for total particulates emitted.[3,4]

Wet Process [5]

The wet process is the same as the dry process, except that a slurry is produced initially. Particulate emissions were obtained by the EPA sampling train method at two cement plants using the wet process and employing, respectively, baghouses and electrostatic precipitators. Samples were taken at the exits of the control equipment, and emission factors (Table 4-1) were estimated as described for the dry process.

PROCESSING OR USES OF BERYLLIUM AND ITS COMPOUNDS

Beryllium Alloys [1,6,7]

The beryllium-copper alloy from the production plants is usually stamped and drawn into finished shapes. The emission factor given in Table 4-1 was estimated by Davis.[1] It is not known whether control equipment was employed.

Another use for beryllium-copper ingots is in the production of beryllium-copper molds for plastic casting. The process involves melting down 2 percent beryllium-copper ingots in a crucible inside a furnace (1040°C). After melting, the molten material is poured into molds and cooled. Emissions are controlled by venting the areas of concern to a baghouse.

A typical plant was visited, and an EPA particulate train was employed at the inlet and outlet of the baghouse.[8] The samples were analyzed by flame atomic absorption.[9] Emission factors based on the analytical results are shown in Table 4-1.

Ceramics [1]

A typical ceramic process begins with beryllium oxide and other materials being mixed in a large floor cistern containing water. The next steps are milling, wet screening, and firing to produce a glazed product. Emissions can result from handling before processing and from machining

the finished product. Emissions are controlled by hoods, central ventilation ducts, and absolute filters. The emission factor presented in Table 4-1 is based on estimates by ceramic manufacturers.

Rocket Propellants [1]

Propellants that contain beryllium are mixed with other propellant ingredients, vacuum cast, cured, and sometimes machined. The manufacture of beryllium-containing propellants has virtually been discontinued, however, and this emission source can therefore be neglected.

Beryllium Metal Fabrication [1]

Beryllium metal is generally fabricated for use in aircraft, computer, and spacecraft parts. The operations usually consist of turning, milling, drilling, reaming, grinding, honing, sawing, and other high-precision machining. Emissions, usually a fine particulate mist, can occur during any of the operations described.

Emissions are controlled by some type of ventilation system, usually coupled with a baghouse or cyclone. The emission factor given in Table 4-1 was obtained from questionnaire data.

FUEL COMBUSTION

Coal [1,8-11]

Stack analyses for beryllium have been conducted at several power plants that burn coal as the fuel. The sampling was done with an EPA sampling train, and analysis was by emission spectrometry. The probe for the sampling train was placed in the stack in the area after the scrubber or electrostatic precipitator control equipment. Four plants were studied, average emission values for two or three sample runs were obtained, and the emission factors presented in Table 4-2 were calculated. The emission factors ranged from 0.0001 to 0.002 kilogram per 1000 kilograms of coal burned. The content of beryllium in the coals burned was also analyzed by emission spectrometry. The values ranged from 1 to 2 parts per million with an average value of 1.3 parts per million.[8,9]

Two studies of coal bed samples from various parts of the United States were conducted by a geological survey team. The samples were ashed, and the ash was analyzed by a quantitative spectrochemical technique for beryllium and other trace metals. The emission factors for this work are based on the percent ash of the coal and the weight percent of the beryllium found in the ash, assuming 65 percent of the ash is fly ash and assuming no controls.[1,10,11] The beryllium content reported in Table 4-2 is the amount in the coal, not the amount in the ash (see Reference 10).

Oil [12,13]

The content of beryllium in oils has not been well defined. An emission factor for residual oil based on an estimate given by Davis[1] is included in Table 4-3.

One oil burning power plant was visited, and particulate samples were obtained with an EPA sampling train. The particulate samples were then analyzed by emission spectrometry for beryllium. The emission factor given in Table 4-3 is based on the percent beryllium found in the sample and the particulate emission factor derived from the sampling train results.[12]

Several oil samples were analyzed by flame atomic absorption of beryllium. All samples analyzed showed beryllium below the detectable limit (less than 0.3 part per million) of the technique. On improving the technique, two No. 6 residual oils showed beryllium to be present at 0.1 part per million. The emission factor given in Table 4-3 is based on the amount of beryllium present, 944 grams per liter of oil, and an assumed 100 percent combustion factor.[13]

Both values based on analytical results in Table 4-3 agree reasonably well with the value estimated by Davis.[1]

WASTE INCINERATION [14,15]

Products that contain beryllium and its compounds can become atmospheric emissions as a result of waste incineration. There are two types of sewage sludge incinerators: multiple hearth furnaces and fluidized bed incinerators. The major difference between the incinerators is that in the multiple hearth all ash leaves through the bottom, but in the fluidized bed, ash is carried overhead and removed by a scrubber. For sewage sludge incinerators, a wet scrubber (impinjet, inertial jet, or venturi) control device is part of the process.[14]

Three sewage sludge incinerators and one municipal incinerator were visited by an EPA sampling team. For sewage sludge incinerators, particulate samples were collected and analyzed for beryllium by emission spectrography. Beryllium at one sewage sludge incinerator was found to be below the detectable level of the analytical techniques. Emission factors presented in Table 4-4 are

based on the weight percent of beryllium (micrograms per gram) found in the samples from the other two incinerators.[14]

The same sampling techniques were used for the municipal incinerator, but the particulates collected were analyzed by emission spectrometry. The emission factor was calculated by the same method as used for sewage sludge units.[15]

OTHERS

Foundries and steel mills may also be important emission sources for beryllium. However, not enough information is available to obtain emission factors.

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Table 4-1. EMISSION FACTORS FOR BERYLLIUM FROM INDUSTRIAL AND SOLID WASTE INCINERATION SOURCES

Source[a]	Emission factor	Emission factor symbol[b]
Mining	0.1 kg/10^3kg (0.2 lb/ton) of Be produced	E
Production of beryllium metal and its compounds, overall value[c]	15 kg/10^3kg (30 lb/ton) of Be produced	CAA (?)
Cement plants[c]		
Dry process		
Feed to raw mill[d]	0.00002 kg/10^6kg (0.00003 lb/1000 tons) of feed	ES (1)
Wet process		
Kiln[e,f]	0.001 kg/10^6kg (0.002 lb/1000 tons) of feed	ES (1)
Clinker cooler[e]	0.0004 kg/10^6kg (0.0008 lb/1000 tons) of feed	ES (1)
Clinker cooler[g]	0.0005 kg/10^6kg (0.0009 lb/1000 tons) of feed	ES (1)
Processing or uses of beryllium and its compounds		
Beryllium alloys (stamped and drawn)[h]	0.05 kg/10^3kg (0.1 lb/ton) of Be processed	E
Beryllium alloys (molding)		
Uncontrolled	0.005 kg/10^3kg (0.01 lb/ton) of alloy melted	CAA (4)
After a baghouse	0.0002 kg/10^3kg (0.0004 lb/ton) of alloy melted	CAA (2)
Ceramics[c]	0.5 kg/10^3kg (1 lb/ton) of Be processed	Q
Rocket propellants	Negligible	–
Beryllium metal fabrication[c]	0.05 kg/10^3kg (0.1 lb/ton) of Be processed	Q

[a] Uncontrolled unless otherwise specified.
[b] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.
[c] Controlled emission factor.
[d] Exit from baghouse.
[e] Exit from electrostatic precipitator.
[f] At another plant, beryllium emissions from the kiln were below the detection limit of the analytical technique.
[g] Exit from two baghouse collectors in parallel.
[h] It is not known whether this estimate is based on controlled or uncontrolled emissions.

Table 4-2. EMISSION FACTORS FOR BERYLLIUM FROM FUEL COMBUSTION, COAL

Source[a]	Beryllium content, ppm	Emission factor		Emission factor symbol[b]
		kg/10^3kg	lb/ton	
Power plants				
Kansas[c]	2	0.00002	0.00004	EST (2)
South Carolina[d]	—[e]	0.00001	0.00002	EST (6)
Illinois[d]	1	0.00002	0.00003	EST (2)
Michigan[d]	1	0.00001	0.00002	EST (2)
Coal beds				
Maryland	2.4	0.002	0.003	SC (6)
Ohio	2.6 (0.5 to 5.1)	0.0023	0.0046	SC (137)
Pennsylvania	2.8 (1.8 to 3.7)	0.0013	0.0026	SC (13)
Alabama	2.2 (0.5 to 4.6)	0.0017	0.0033	SC (70)
Georgia	1.6 (0.8 to 2.2)	0.001	0.002	SC (6)
Kentucky-east	4.4 (0.1 to 19)	0.0035	0.0069	SC (87)
Kentucky-west	2.4 (0.5 to 5.0)	0.0022	0.0044	SC (313)
Tennessee	2.8 (0.6 to 11)	0.0012	0.0023	SC (29)
Virginia	1.2 (0.5 to 1.9)	0.0005	0.001	SC (6)
West Virginia	1.3 (0.2 to 3.6)	0.0012	0.0023	SC (25)
Illinois	2.0 (0.5 to 5.7)	0.0018	0.0036	SC (565)
Indiana	4.5 (1.4 to 7.6)	0.0046	0.0091	SC (178)
Arkansas	1.8 (0.1 to 10.2)	0.0010	0.0020	SC (25)
Iowa	3.6 (2 to 5.1)	0.0025	0.0049	SC (22)
Missouri	3.8 (0.5 to 10.4)	0.0039	0.0078	SC (57)
Oklahoma	1.6 (0 to 3.5)[f]	0.0011	0.0022	SC (49)
Montana	2.4 (0 to 9.1)[f]	0.0027	0.0054	SC (118)
North Dakota	0.8 (0 to 4.0)[f]	0.00055	0.0011	SC (56)
Wyoming	1.4 (0 to 12.7)[f]	0.0023	0.0046	SC (75)
Colorado	0.6 (0 to 1.8)[f]	0.0017	0.0033	SC (98)
Utah	0.3 (0 to 0.6)[f]	0.0003	0.0006	SC (33)
U.S. average (coal beds)	2.2	0.0019	0.0037	SC (1875)

[a] Uncontrolled unless otherwise specified.

[b] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.

[c] Exit from limestone wet scrubber.

[d] Exit from electrostatic precipitator.

[e] Not reported.

[f] Zeros indicate below detectable level of analytical technique employed.

Table 4-3. EMISSION FACTORS FOR BERYLLIUM FROM FUEL COMBUSTION, OIL

Source	Beryllium content, ppm	Emission factor		Emission factor symbol[a]
		kg/10^3 liters	lb/10^3 gal.	
Residual oil	0.08	0.00008	0.0007	E
Power plant, Connecticut[b]	0.024	0.00002	0.0002	EST (2)
Residual No. 6	0.1	0.00009	0.0008	CAA (2)

[a] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.

[b] Exit from electrostatic precipitator.

Table 4-4. EMISSION FACTORS FOR BERYLLIUM FROM WASTE INCINERATION

Source	Emission factor		Emission factor symbol[a]
	kg/10^6kg of waste burned	lb/10^3 tons of waste burned	
Sewage siudge incinerator			
Multiple hearth, after wet scrubber	0.001 (0.0005 to 0.002)	0.002 (0.0009 to 0.003)	OES (3)
Fluidized bed, after wet scrubber	0.001 (0.00005 to 0.001)	0.002 (0.0001 to 0.002)	OES (3)
Municipal incinerator, uncontrolled	0.02	0.03	EST (1)
Municipal incinerator, after electrostatic precipitator	0.02	0.03	EST (1)

[a] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.

5. CADMIUM

MINING OF ZINC-BEARING ORES[1]

Cadmium does not occur as a free mineral in nature. It is found with zinc ores and other metal ores that contain zinc compounds. The most important mineral is sulfide greenockite, which is found with zinc sulfide ores.

The processing is somewhat the same in all mining operations — ore removal, ore handling, crushing, grinding, and concentration. Concentration is done by means of a flotation process in this case.

Cadmium emissions are mainly due to wind losses from tailing piles. No controls are employed in such operations. The emission factors (which include operations and tailing piles) for mining are presented in Table 5-1.

METALLURGICAL INDUSTRY[1,2,3]

Zinc, Lead, and Copper Smelters

Table 5-1 contains the emission factors for cadmium for the metallurgical industry. The sources of cadmium in this industry are mainly zinc, lead, and copper smelters.

In the production of metallic zinc, the sulfur present in the ore is removed by multiple hearth (920°C) or Ropp roasting, followed by sintering (1200°C). Metallic zinc is then produced in the next step, which is a horizontal or vertical retort smelting process. Roasting is sometimes followed by an electrolytic process. Most of the cadmium is emitted in the roasting and sintering process, and particulates are normally collected in baghouses and/or electrostatic precipitators. Cadmium compounds emitted are cadmium chloride (roasting) and cadmium oxide (sintering and smelting). Refining of the cadmium collected in the control equipment begins with a sulfuric acid leach plus the addition of an oxidizing agent. Next, cadmium is distilled in the conventional horizontal retort (910°C) and then condensed as metallic cadmium.[3] The emission factors for both processes (zinc smelter and refining) are shown in Table 5-1.[1]

Emissions from lead and copper smelters also contain cadmium as a result of zinc and associated cadmium present in the ores processed. The emissions result from the roasting operation. As in zinc production, cadmium is collected in baghouses on electrostatic precipitators. The cadmium content in the collected material is low, so it is recycled many times before the cadmium is refined. The recycling allows opportunity for major quantities of the cadmium to escape.

Emission factors for lead and copper smelters are presented in Table 5-1. The factors do not differentiate between emitted cadmium vapor and particulate matter.

Secondary Copper[1]

Automobile radiators contain copper that has been hardened by the use of about 0.2 percent cadmium. When the radiators are melted for copper recovery, the manufacturers do not recover the cadmium. The emission factor given in Table 5-1 is based on the 0.2 percent value and the amount of secondary copper obtained from radiators.

Secondary Lead[4]

The production of secondary lead mainly consists of melting down lead batteries, lead oxide drosses, recycled ducts, and metal scrap. The process consists of melting the feed in a reverberatory or blast furnace (930°C). The molten mass is then transferred to holding and refining kettles and poured into ingots on a casting line.

Plants that employ controls usually use some type of cooling system followed by cyclones, baghouses, and/or scrubbers. Emissions of particulate matter result from all of the processes described, but only the exit stream from a furnace has been studied. Four plants were visited, and particulate matter collected by an EPA sampling train was analyzed by optical emission spectroscopy. Cadmium was present in the samples from two reverberatory furnaces. The samples from two blast furnaces showed cadmium below the minimum limit of the technique employed.

Emission factors presented in Table 5-1 are based upon the analytical results, process conditions, and emission factors calculated for particulate from probe and filter catch of the EPA train.

Galvanized Metals [1]

Galvanized metal and steel scrap that is melted down will contain some cadmium as an impurity in the zinc galvanizing metal. Zinc used in galvanizing averages about 3.7 kilograms per 1000 kilograms of steel produced. Cadmium content in the zinc (for galvanizing) is about 0.04 percent. No cadmium is reported to be recovered; and the emission factor given in Table 5-1 is based on the percent present.

CEMENT PLANTS

Cement manufacturing processes are described in Chapter 4. Cadmium emissions from the processes are due to the presence of cadmium as an impurity in the initial chemicals used to produce cement. Emissions from both dry and wet process cement plants can result from all of the processes described.

Dry Process [5]

Two plants using the dry process were visited, and particulate samples were obtained by the EPA sampling train method. Baghouses at both plants were employed as air pollution control equipment. The probes for the sampling train were placed in the stack area after each baghouse. Stacks from which samples were taken included the kilns (at one plant only), raw mill grinding systems, and finish mill grinding systems. Some of the samples were analyzed by emission spectroscopy for trace metals. The emission factors (Table 5-1) were based on percent of cadmium present in the sample and the emission factor calculated for total particulates.

Wet Process [6]

Particulate emissions were obtained from the kilns, clinker cooler, and finishing mill of three plants that employed the wet process. The same analytical techniques described in the dry process section were employed, except that one sample was analyzed by spark source mass spectrograph and optical emission spectrograph. Sampling was done at the exits of the baghouses or electrostatic precipitators employed at the individual plants. Two samples analyzed (by emission spectroscopy) at one plant showed cadmium below the detectable level. The samples came from a kiln and clinker cooler, each controlled by an electrostatic precipitator. Emission factors (Table 5-1) were calculated as described in the section for the dry process.

PROCESSING OR UTILIZATION OF CADMIUM [1,7]

Processing or utilization of cadmium and its compounds is divided into six main categories: (1) electroplating, (2) pigments, (3) plastics, (4) alloys, (5) batteries, and (6) miscellaneous. Table 5-2 gives emission factors for each.

Electroplating [1]

Cyanide baths are used for almost all commercial plating. Emissions from the electroplating industry for cadmium are negligible. The process involves setting up articles to be coated as cathodes and the cadmium metal as an anode. As electricity is passed through the bath, the metal is coated with cadmium. If gassing rates are high in the bath, emissions could become quite significant. However, this process is quite efficient, and low gassing rates prevail. On the average, electroplated iron and steel contain about 0.025 kilogram of cadmium per 1000 kilograms of steel or iron produced.

Pigments [1]

Cadmium is used in pigments as a coloring agent. The two compounds of importance are cadmium sulfide and sulfoselenide.

Cadmium sulfide is prepared in many ways. One process involves heating cadmium oxide with suflur and another dissolving cadmium oxide in sulfuric acid and then precipitating the sulfide from the solution with hydrogen sulfide.

Cadmium sulfoselenide lithopone is prepared by mixing solutions of cadmium sulfate and barium sulfide to obtain cadmium sulfide and barium sulfate. The shade of color is then determined by a calcining process. Cadmium sulfoselenide is prepared by adding selenium to a solution of barium sulfide or nitrate, reacting these with cadmium sulfate, and calcining with sulfur to remove unreacted selenium. Emissions from pigment processing occur mainly from drying the calcinated powder. For all processes described, bag filters are normally employed as air pollution control devices. The emission factor in Table 5-2, based on a material balance analysis, is therefore considered a controlled emission factor.

Plastics [1]

Cadmium use in plastics is important and is growing. Cadmium is used in plastics as a coloring agent and sometimes as a stabilizer (as a barium-cadmium compound). During processing of the stabilizers, cadmium oxide is placed in a sealed reactor to react with fatty acids to form cadmium soaps. Emissions from this process only occur in handling of the oxide before the reaction.

Since all plants investigated stated they used bag filters to control emissions, the emission factor in Table 5-2 is considered a controlled emission factor.

Alloys [1,3,8]

In the United States, a large number of companies produce alloys containing cadmium. Their range of usage is from 450 to 68,000 kilograms. Their products are largely low-melting solders, bearing alloys, and brazing alloys. Aluminum solders are cadmium-zinc alloys in which the composition of cadmium varies from 10 to 95 percent by weight.[3] Brazing alloys contain between 5 and 18 percent cadmium. Low-melting or fusible alloys have a cadmium range of 8 to 40 percent by weight.[8] Bearing alloys in which nickel or silver and copper are alloyed with cadmium contain 99 percent cadmium.[3] In production of these alloys, cadmium is applied by vacuum deposition, dipping, spraying, or electrodeposition (already discussed).[3] The extent of the application of air pollution control equipment in this industry for these specific applications is not known. The emission factor in Table 5-2 is based upon manufacturers' estimates and is assumed to be for a controlled operation.[1]

Batteries (Ni-Cd) [1]

Nickel-cadmium batteries are used extensively. The battery grids of both positive and negative plates consist of sintered carbonyl nickel powder. The positive plate is nickel oxide and the negative plate is cadmium. The process for producing these plates is mainly sintering and electrochemical depositing. The emission factor in Table 5-2 is based upon manufacturers' estimates of emissions, which are generally uncontrolled.

Miscellaneous [1]

Miscellaneous uses in which cadmium is processed include x-ray screens, cathode ray tubes, nuclear reactor components, etc. The emission factor in Table 5-2 can be used as a rough approximation for these other uses.

CONSUMPTIVE USES [1,9,10]

Emission factors (Table 5-3) for consumptive (i.e., nonmanufacturing) uses of cadmium have been estimated for rubber tire wear, fungicides, superphosphate fertilizers, motor oil, and cigarettes. In tires, cadmium sulfide is used as a curing agent. Cadmium salts are used in fungicides on golf courses. Cadmium phosphate is used in fertilizers. Cadmium is not added to motor oils, but analysis of motor oils has shown an average content of about 0.5 part per million.[1,9,10]

FUEL COMBUSTION

Oil [1,11-14]

Foreign crude and residual oils and U.S. crude oils have been analyzed by neutron activation and flame atomic absorption.[12,14] Three of six No. 6 fuel oils analyzed by neutron activation contained cadmium (3 to 5 parts per million). Cadmium in the other three samples was below detectable levels of the technique. All of 20 No. 6 fuel oil samples analyzed by flame atomic absorption had cadmium contents below the 0.4 part per million detection limit of the technique. Eight foreign crude oils from different sources were also analyzed by the two techniques; only one (analyzed by neutron activation) showed any cadmium present. Cadmium was below detectable levels for all of seven U.S. crude oils analyzed by neutron activation.

In another study, a diesel oil and a heating oil were analyzed by emission spectroscopy, and the cadmium contents ranged from about 0.07 to 0.1 and 0.4 to 0.5 part per million, respectively.[11]

Emission factors for oil combustion are presented in Table 5-4. The factors calculated are based upon cadmium content of the oils analyzed, an assumed 100 percent combustion factor, and a density of 850 (crude) and 944 (residual) kilograms per liter for oil. No data are available as to the particle size of cadmium or the physical condition (vapor or particulate) of cadmium upon emission. Average values based on the analytical results are not given because it seems cadmium may not be present in all the oil types analyzed.

Coal [15,16]

Fly ash samples from four power plants were analyzed by emission spectrometric methods to determine trace metals present.[15,16] The samples were all taken by an EPA sampling train. The probe of the train was placed in the stack after the electrostatic precipitator or wet scrubber control

equipment. Cadmium (20 to 170 μg/g) was present in only 4 of the 14 samples analyzed. The coal burned at these plants was also analyzed for cadmium, but because of the limits of the analytical procedure, cadmium detection was uncertain. The analyses indicated that not all coal-burning boilers emit cadmium. The emission factors presented in Table 5-4 are based on process conditions and the amount of cadmium found in the fly ash samples.

Gasoline [3]

One out of six gasolines analyzed by emission spectrographic analysis contained cadmium, about 6 parts per billion. Since only one of the gasolines analyzed contained cadmium, no emission factor is given for gasoline combustion.

WASTE INCINERATION [1,17-19]

Emission factors for sewage sludge, municipal, sewage sludge-mixed refuse, and waste lubrication oil [19] incineration are given in Table 5-5.

There are two main types of sewage sludge incinerators: multiple hearth and fluidized bed. Both incinerators have similar design, with the only major difference being that ash is removed from the bottom of the multiple hearth furnace, but in the fluidized bed, all the ash is carried overhead and is removed by a scrubber. Scrubbers (impinjet, inertial jet, and venturi) are a part of the process design of sewage sludge incinerators.

Three sewage sludge incinerations were visited, and particulate samples were obtained by the EPA sampling train method. The samples were analyzed by emission spectroscopy. [17] One incinerator that handled mixed refuse and sewage sludge was visited, and particulate samples were collected using a null balance probe. [18] The samples were analyzed by atomic absorption for cadmium. The emission factors presented in Table 5-5 are based on amounts of cadmium found in the particulate matter analyzed. The overall value for the municipal incinerator in Table 5-5 was estimated in Reference 1 for an uncontrolled process. It is presented here for comparison with the source test data and should not be used for emission estimates.

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Table 5-1. EMISSION FACTORS FOR CADMIUM FROM INDUSTRIAL SOURCES

Source[a]	Emission factor	Emission factor symbol[b]
Mining of zinc-bearing ore[c]	0.0005 kg/10^3kg (0.001 lb/ton) of Zn or 0.1 kg/10^3kg (0.2 lb/ton) of Cd mined	E
Zinc smelters[d]	150 kg/10^3kg (300 lb/ton) of Cd charged or 1.0 kg/10^3kg (2.0 lb/ton) of Zn produced	PV, MV, Q
Copper smelters	650 kg/10^3kg (1300 lb/ton) of Cd charged or 0.4 kg/10^3kg (0.07 lb/ton) of Cu produced	PV, MV, Q
Lead smelters	650 kg/10^3kg (1300 lb/ton) of Cd charged or 0.1 kg/10^3kg (0.2 lb/ton) of Pb produced	PV, MV, Q
Cadmium refining units	13 kg/10^3kg (25 lb/ton) of Cd produced	PV, MV, Q
Secondary copper[c]	2 kg/10^3kg (4 lb/ton) of Cu scrap	E
Secondary lead		
Reverberatory furnace[e]	0.05 kg/10^6kg (0.1 lb/10^3 tons) of Pb[i]	ES (3)
Reverberatory furnace[f]	0.2 kg/10^6kg (0.4 lb/10^3 tons) of Pb	ES (2)
Steel scrap (galvanized metal)[c]	0.001 kg/10^3kg (0.003 lb/ton) of steel	E
Cement plants		
Dry process		
Kiln[g]	0.2 kg/10^6kg (0.3 lb/10^3 tons) of feed	ES (1)
Raw mill[g]	0.00005 kg/10^6kg (0.0001 lb/10^3 tons) of feed	ES (1)
Air separator after raw mill[g]	0.0005 kg/10^6kg (0.0009 lb/10^3 tons) of feed	ES (1)
Feed to raw mill[g]	0.0002 kg/10^6kg (0.0003 lb/10^3 tons) of feed	ES (1)
Feed to finish mill[g]	0.003 kg/10^6kg (0.0005 lb/10^3 tons) of feed	ES (1)
Wet process		
Kiln[h]	0.1 kg/10^6kg (0.2 lb/10^3 tons) of feed	ES (1)
Raw mill[g]	0.01 kg/10^6kg (0.02 lb/10^3 tons) of feed	ES (1)
Clinker cooler[g]	0.00005 kg/10^6kg (0.0001 lb/10^3 tons) of feed	OES,SSMS (1)

[a] In this table, sources are controlled unless otherwise specified.
[b] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.
[c] Uncontrolled emission factor.
[d] Factors should not be used for electrolytic process.
[e] Exit from a cooling system, three cyclones, and a baghouse (121° C).
[f] Exit from a cooling system, cyclone, manifold, hopper, and baghouse (93° C).
[g] Exit from baghouse.
[h] Exit from electrostatic precipitator. At another plant using an electrostatic precipitator, no cadmium was using ES analytical method.
[i] Range, 0.02 to 0.1 kg/10^6kg (0.04 to 0.2 lb/10^3ton).

Table 5-2. EMISSION FACTORS FOR PROCESSES INVOLVING CADMIUM

Source [a]	Emission factor, kg/10^3kg (lb/ton) of cadmium charged	Emission factor symbol [b]
Pigments [c]	8 (15)	MB
Plastic stabilizers [c]	3 (6)	PV
Alloys and solders [d]	5 (10)	Q
Batteries (Ni-Cd)	1 (2)	Q
Miscellaneous (x-ray screens, cathode ray tubes, nuclear reactor components, etc.)	1 (2)	E

[a] Emission are uncontrolled unless otherwise specified.

[b] Defined in Table 1-1.

[c] Controlled emissions (bag filters).

[d] Controlled emissions.

Table 5-3. EMISSION FACTORS FOR CONSUMPTIVE USES OF CADMIUM

Source [a]	Emission factors	Emission factor symbol [b]
Rubber tire wear	0.003 kg/10^6km (0.01 lb/10^6 vehicle miles)	E
Fungicides	0.02 kg/10^3 liters (0.05 lb/10^3 gal.) of spray	E
Superphosphate fertilizers	0.0001 kg/10^3kg (0.0002 lb/ton) of fertilizer	E
Motor oil consumption (in vehicle)	0.0006 kg/10^6km (0.002 lb/10^6 vehicle miles)	UK
Cigarettes	16.0 µg/20 cigarettes	S (15)

[a] All sources are uncontrolled.

[b] Defined in Table 1-1; number in parentheses indicates number of samples analyzed.

Table 5-4. EMISSION FACTORS FOR CADMIUM FROM FUEL COMBUSTION

Source [a]	Cadmium content, ppm	Emission factor	Emission factor symbol [b]
Heating oil (residual assumed)	0.4 to 0.5	0.004 to 0.0005 kg/10^3 liters (0.003 to 0.004 lb/10^3 gal.) of oil	ES (2)
Diesel oil	0.07 to 0.1	0.00007 to 0.00009 kg/10^3 liters (0.0006 to 0.0008 lb/10^3 gal.) of oil	ES (3)
Foreign No. 6 residual fuel oil			
Virgin Islands	5	0.005 kg/10^3 liters (0.04 lb/10^3 gal.) of oil	NA (1)
Virgin Islands (different oil field)	< 0.4 [e]	—	CAA (3)
Curacao, N.A.	4	0.004 kg/10^3 liters (0.03 lb/10^3 gal.) of oil	NA (1)
Trinidad	3	0.003 kg/10^3 liters (0.02 lb/10^3 gal.) of oil	NA (1)
Venezuela	< 0.4 [e]	—	CAA (10)
Coal, power plant, Kansas [c]	— [f]	0.1 kg/10^6kg (0.2 lb/10^3 tons) of coal burned [g]	EST (2)
Coal, power plant, Michigan [d]	— [e]	0.5 kg/10^6kg (1 lb/10^3 tons) of coal burned [g]	EST (2)

[a] Uncontrolled emissions unless otherwise specified.

[b] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.

[c] Exit from limestone scrubber.

[d] Exit from electrostatic precipitator.

[e] Below detectable limits of techniques.

[f] Not reported.

[g] Based on ash samples.

Table 5-5. EMISSION FACTORS FOR CADMIUM FROM WASTE INCINERATION

Source [a]	Emission factor	Emission factor symbol [b]
Sewage sludge incinerators		
Multiple hearth [c,d]	0.004 kg/10^3kg (0.007 lb/ton) of solid waste incinerated [g]	OES (3)
Fluidized bed [c]	0.0002 kg/10^3kg (0.003 lb/10^3 tons) of solid waste incinerated	OES (2)
Municipal incinerator		
Refuse only [c]	0.4 kg/10^6kg (0.8 lb/10^3 tons) waste incinerated	CAA (3)
Refuse and sludge [c]	0.3 kg/10^6kg (0.6 lb/10^3 tons) waste incinerated	CAA (3)
Overall value for uncontrolled solid waste incineration (municipal) [e]	0.0002 kg/10^3kg (0.003 lb/ton) of solid waste incinerated	E
Lubricating oil [f]	0.0002 kg/10^3 liters (0.002 lb/10^3 gal.) of oil	UK

[a] In this table, emissions are controlled unless otherwise specified.

[b] Defined in Table 1-1; number in parentheses indicates number of samples analyzed.

[c] Exit from wet scrubber.

[d] Cadmium ratio of metal in particulate to metal in sludge was 2.6.

[e] This emission factor is presented for comparison only; it should not be used for emission estimates.

[f] Emissions of cadmium oxides.

[g] Range, 0.0005 to 0.01 kg/10^3kg (0.001 to 0.02 lb/ton).

6. MANGANESE

MINING [1]

Most ore mined for manganese in the United States is manganiferous ore (5 to 35 percent manganese). Some manganese ore (35 or more percent manganese) is also mined in the United States, but this ore is usually imported from foreign countries. Manganese is also found in iron ores but is not recovered from this ore because of economical reasons.

Processing at mining operations varies considerably. All operations have crushing, screening, and washing steps, and some also have concentrating equipment, which many times will include sintering and nodulizing equipment. Atmospheric emissions result from ore handling, crushing, and wind losses from tailings. The emission factor presented in Table 6-1 is based upon information obtained from mine operators. No controls are used in the mining of ores containing manganese.

PRODUCTION OF MANGANESE METAL [1]

An electrolytic process is used to produce pure manganese metal. The principal steps are grinding, roasting the ore, leaching, purification of the leach liquor, and electrodeposition of the manganese. In the roasting step, the object is to convert all of the manganese into the oxide form. After grinding and roasting, the product is leached in leach liquor that is first acidic but is later neutralized. The neutralizing enables the extraction of about 98 percent of the manganese in the ore as a result of the precipitation of iron and aluminum hydroxides. The resultant product must be further purified before electrolysis. The first step in purification is the addition of hydrogen sulfides or ammonium sulfide to precipitate the sulfides and some of the impurities. The second step involves the addition of iron (copperas), which oxidized the iron at a pH of 6.5 to 7.0 and precipitates ferric hydroxide. The other impurities are removed with the hydroxide. The purified solution is placed in the cathode compartment of an electrolytic cell where the manganese is deposited.

Emissions result from handling, grinding, and roasting of the ore. The emission factor given in Table 6-1 is based on manufacturers' estimates.

PRODUCTION OF MANGANESE ALLOYS [1]

Manganese ores are also used in the production of ferromanganese, siliconmanganese, and spiegeleisen. Ferromanganese is produced in blast and electric furnaces, while siliconmanganese and spiegeleisen are produced in electric furnaces.

Ferromanganese - Blast Furnace [1,2]

The blast furnace is a large refractory-lined chamber into which the manganese ore is charged. About 65 percent of the ferromanganese is produced from blast furnaces. Particulate emissions from the blast furnaces are about 205 kilograms per 1000 kilograms of ferromanganese produced,[2] of which about 20 percent is manganese.[1] The emission factor is based on this information and is considered to be uncontrolled.

Ferromanganese - Electric Furnace [1]

Electric furnaces are furnished with heat from arc type electrodes in the roof of the furnace. Emissions result from the furnace, tapholes in the furnace, handling, and mixing. The emission factor (uncontrolled) presented in Table 6-1, estimated by Davis,[1] includes nonmelting operations as well.

Siliconmanganese - Electric Furnace [1]

In the production of siliconmanganese, emissions result from the same sources as ferromanganese production in electric furnaces. The emission factor presented in Table 6-1 is based upon an internal EPA report referenced by Davis.[1]

PROCESSING OF MANGANESE AND ITS COMPOUNDS [1]

About 90 percent of the manganese used in the United States is consumed by the steel industry. The remainder is used to make cast iron, nonferrous alloys, batteries, chemicals, and other products.

Steel Production [1]

Manganese is used in the production of almost every grade of steel. There are three main functions

of manganese in the steel industry. It is a deoxidizer and cleanser of molten steel, it improves the hot-working properties of the steel, and it is an important alloying agent. About 6.6 kilograms of manganese are consumed per ton of steel produced.[1]

The basic step in the production of steel is the reduction of impurities in the blast furnace. Further purification takes place in open hearth, basic oxygen, or electric furnaces. Other operations include ore crushing, handling, sintering, pelletizing, and scarfing.

Blast Furnace [1,2]

Manganese is part of each principal ingredient charged into the blast furnace. It is present in the iron and manganiferous ore (or other manganese type ores), in the scrap, and in the recycled slag. Pig iron from the blast furnace will contain about 70 percent of manganese initially present in the charge. The remaining 30 percent is in the slag and gases that are produced. In most cases, the gas by-product is cleaned (about 97 percent efficiency) and used as a fuel. The emission factor presented in Table 6-1 is for an uncontrolled source and an estimated 0.5 percent[1] of manganese present in the particulate material (75 kilograms per 1000 kilograms of pig iron produced).[2]

Open Hearth Furnace [1,2,3]

Using pig iron (about 55 percent) from the blast furnace, "home scrap," and purchased scrap, steel is produced in an open hearth furnace. The primary objective of the furnace is to reduce impurities. Molten pig iron is added to the furnace, then ore and lime boil are added. Next, a working period is employed to lower the phosphorus, sulfur, carbon (to desired level), and oxygen contents. During this work period, manganese losses are at a maximum (70 to 80 percent in the fume and slag).[1] Emissions for uncontrolled open hearth furnaces with and without oxygen lancing are 11 and 6 kilograms of particulate per 1000 kilograms of steel produced, respectively.[2] Using qualitative data (by emission spectrography), which indicated about 0.5 percent manganese present in the particulate matter, emission factors were estimated as indicated in Table 6-1.[3]

Basic Oxygen Furnace [1,2]

This furnace is a refractory-lined, cylindrical vessel that is mounted on trunions. The furnace is charged in the vertical, and a stream of oxygen, supplied from overhead, is shot downward into the converter. The oxygen causes agitation and mixing action, which results in increased fume emissions. For uncontrolled operations, the approximate amount of particulate matter emitted per 1000 kilograms of steel produced is 23 kilograms.[2] It has been estimated that about 3.2 percent of this emission is manganese (4.4 percent Mn_3O_4).[1] The uncontrolled emission factor is given in Table 6-1.

Electric Furnace [1,2]

An electric furnace is a refractory-lined, cylindrical vessel with large carbon electrodes passing through the roof of the furnace. In charging this type of furnace (preheated), the top is opened to allow cold metal to be introduced. Large amounts of fume result, and the fumes increase throughout the process. Particulate emissions for oxygen lancing and no lancing are 5.5 and 3.5 kilograms per 1000 kilograms of steel produced, respectively.[2] Using an estimated 3.1 percent of manganese present in the particulate, uncontrolled emission factors, presented in Table 6-1, were calculated.[1]

Cast Iron [1,2]

Manganese is added to the cupola in the production of cast iron to reduce the sulfur content in the final product. The charge into the cupola contains coke, scrap, and pig iron, all of which contain manganese. The manganese either reacts with the air introduced into the cupola to form oxides or with the sulfur to form manganese sulfide. These compounds are removed in the slag. The manganese present in the particulate material is about 2 percent.[1] The emission factor in Table 6-1 was calculated from the uncontrolled particulate emission factor (8.5 kilograms per 1000 kilograms of metal charged)[2] and the percentage of manganese present.

Welding Rods [1]

Some welding rods and coatings contain manganese. Aluminum welding rods contain about 1.5 percent manganese, and coatings of other rods contain about 10 percent manganese. Manganese is added to aluminum welding rods as a general purpose alloy.

To make aluminum welding rods, aluminum-rich alloy ingot containing the manganese is added to a charge of aluminum and alloy scrap in a reverberatory furnace (at 760°C). After melting, the material flows to a trough and is tapped and poured into ingots. The ingots are cooled, and then reheated and rolled in a blooming mill. The product is sent to a rod mill and finished by forging, swaging, or drawbenching.

Emissions of manganese result from the furnace and the hot ingots. The emission factor in Table 6-1 is based on information obtained from industrial sources.

Nonferrous Alloys [1]

Manganese is alloyed with nonferrous metals such as aluminum, magnesium, copper and zinc, and copper and nickel. Aluminum-manganese alloys will contain about 25 percent manganese. Magnesium is alloyed with manganese chloride. Bronze, produced from manganese alloyed with copper and zinc, contains up to about 3.5 percent manganese. The emission factor presented in Table 6-1 is based upon industrial sources.

Batteries [1]

Manganese dioxide is used as a depolarizing agent in the dry cell battery. Manganese dioxide, calcined manganese, graphite carbon black, ammonium chloride, and vita film are first added to a ball mill. The ingredients are then wet mixed, pulverized, and fed into battery cases in a paste filling machine. To produce the final battery, the battery cases are filled in a filling solution machine. Emissions result mainly from the ball mill and mixing. The emission factor given in Table 6-1 is based upon manufacturers' estimates and is considered uncontrolled.

Chemicals [1]

Manganese ore, mainly the dioxide form, is used in the chemical industry as an oxidizing agent in the production of hydroquinore, potassium permanganate, manganese sulfate, manganese chloride, manganese oxides, and others. The emission factor for the overall chemical industry for the production of manganese chemicals (Table 6-1) is based upon information obtained from various segments of the chemical industry.

Others [1]

Manganese and its compounds are also used in the production of fertilizers, animal and poultry feed, pharmaceuticals, brits, glass, ceramics, coloring effects to face bricks, paint driers, and oxidants. They are also employed in air pollution control, in water treatment, and as an experimental fuel additive. No information is presently available to determine emission factors for these sources.

CEMENT PLANTS

Cement manufacturing processes are described in Chapter 4. Manganese is present in pyrite (as manganese sulfide), and possibly in the limestone, shale, and clay used in the production of cement. Emissions from both dry and wet process cement plants can result from all of the processes described.

Dry Process [4]

Two plants using the dry processing method were visited, and particulate samples were obtained by the EPA sampling train method. Baghouses were employed at both plants as air pollution control equipment. The probes for the sampling train were placed in the stack area after each baghouse. Some of the samples (total catch) were analyzed by emission spectroscopy for trace metals. The emission factors in Table 6-1 were based on percent of manganese present in the sample and the emission factor calculated for total particulates emitted.[4] Cement from one plant was analyzed and found to contain 900 micrograms of manganese per gram of sample analyzed.

Wet Process [5]

Particulate emissions were obtained from three cement plants using the wet process. The same analytical techniques described in the dry process section were employed, except that part of one sample from one plant was analyzed by spark source mass spectrography and optical emission spectrography. Sampling was done at the exits of the baghouses or electrostatic precipitators employed at the individual plants. The emission factor in Table 6-1 was also calculated as described in the section for dry processing.

FUEL COMBUSTION

Coal [1,6,7]

Fly ash samples from five power plants were analyzed by emission spectrometric methods to determine trace metals present.[6,7] The samples were all taken by an EPA sampling train with the probe of the train placed in the stack after the electrostatic precipitator or wet scrubber control equipment. Manganese was present in all samples analyzed. The values of manganese ranged from 40 to 1400 micrograms per gram of sample analyzed with an average value of 465 micrograms per gram. The emission factors presented in Table 6-2 are based upon the percent of manganese present in the fly ash sample analyzed and on emission factors estimated in the studies for particulates (based on the EPA train).

In another study, fly ash samples from six power boilers were analyzed by emission spectrometric methods. Two of the boilers were fired with Illinois

coal, two with Pennsylvania coal, one with Ohio coal, and one with West Virginia and Kentucky coal. Manganese present before fly ash collection was 966 to 3910 micrograms per cubic meter with an average of 1950 micrograms per cubic meter. After collection, the manganese present ranged from 60 to 368 micrograms per cubic meter with an average of 212 micrograms per cubic meter. Using these average values, assuming uncontrolled emissions and 9.9 cubic meters of flue gas per kilogram of coal consumed, the emission factor for this study was estimated (Table 6-2).[1]

Oil [1,8]

Analyses of more than 400 samples of crude and residual oils were obtained from major oil companies and utilities along the east coast of the United States. Almost all of the crude oils contained some manganese (0 to 2000 parts per million).[1] Crude oils from the United States contained manganese in the range of 0.005 to 1.45 parts per million. Residual fuel oils in the United States average about 0.158 part per million. Middle East residual oils contained an average of 0.120 part per million of manganese. Analysis of eight South American residual oils showed no manganese present as a result of the limit of the analytical method employed. Emission factors presented in Table 6-3 are based on the manganese content in the oils, assuming no control, a 100 percent combustion factor, and densities of 850 (crude) and 944 (residual) grams per liter for oil.

In another study, several commercial and residential boiler units were studied. Particulate samples from the units were taken by EPA sampling train (total catch) and analyzed by optical emission spectrometry for trace metals.[8] The emission factors obtained in the study are presented in Table 6-3.

WASTE INCINERATION [9,10]

Emission factors for incineration of sewage and sludge, and solid waste are presented in Table 6-4. There are two main types of sewage sludge incineration: multiple hearth and fluidized bed. Both incinerators have similar designs with the only major difference being that ash is removed from the bottom of the multiple hearth furnace, but in the fluidized bed, all ash is carried overhead and is removed by a scrubber. Scrubbers (impinjet, inertial jet, and venturi) are a part of the process design of sewage sludge incinerators.

Three sewage sludge incinerators were visited, and particulate samples were obtained by the EPA sampling train method. The samples were analyzed by emission spectroscopy and manganese was found in all samples.[9]

The values presented for the solid waste incinerated were based upon samples taken from a large U.S. incineration unit (with a design rate of 363×10^3 kilograms per day). The samples were taken by an EPA sampling train for particulates. Sampling points were located at the inlet and outlet of an electrostatic precipitator. The samples were analyzed by emission spectrometry.[10] The emission factors are based on the manganese content in the samples and the process weight rates for each incinerator.

REFERENCES FOR CHAPTER 6

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Table 6-1. EMISSION FACTORS FOR MANGANESE FROM INDUSTRIAL SOURCES

Source[a]	Emission factor	Emission factor symbol[b]
Mining	0.1 kg/10^3kg (0.2 lb/ton) of Mn mined	Q
Manganese metal production	13 kg/10^3kg (25 lb/ton) of Mn processed	Q
Production of manganese alloys		
Ferromanganese		
Blast furnace[c]	41 kg/10^3kg (82 lb/ton) of ferromanganese produced	E
Electric furnace	12 kg/10^3kg (24 lb/ton) of ferromanganese produced	E
Siliconmanganese, electric furnace	35 kg/10^3kg (70 lb/ton) of siliconmanganese produced	E
Processing of manganese and and its compounds		
Steel production (carbon and alloy steels)		
Blast furnace	0.4 kg/10^3kg (0.8 lb/ton) of pig iron produced	E
Open hearth furnace[d]		
Oxygen lance	0.06 kg/10^3kg (0.1 lb/ton) of steel produced	OES (1)
No lancing	0.3 kg/10^3kg (0.6 lb/ton) of steel produced	OES (1)
Basic oxygen furnace[e]	0.7 kg/10^3kg (1 lb/ton) of steel produced	E
Electric furnace		
Oxygen lance	0.2 kg/10^3kg (0.3 lb/ton) of steel produced	E
No lancing	0.1 kg/10^3kg (0.2 lb/ton) of steel produced	E
Cast iron	0.2 kg/10^3kg (0.3 lb/ton) of metal charged	E
Welding rods	8 kg/10^3kg (16 lb/ton) of Mn processed	Q
Nonferrous alloys	6 kg/10^3kg (12 lb/ton) of Mn processed	Q
Batteries	5 kg/10^3kg (10 lb/ton) of Mn processed	Q
Chemicals	5 kg/10^3kg (10 lb/ton) of Mn processed	Q

Table 6-1 (continued) EMISSION FACTORS FOR MANGANESE FROM INDUSTRIAL SOURCES

Source [a]	Emission factor	Emission factor symbol [b]
Cement plants		
Dry process		
Kiln [f]	0.04 kg/10^6kg (0.07 lb/10^3 tons) of feed	ES (1)
Feed to raw mill [f]	0.005 kg/10^6kg (0.01 lb/10^3 tons) of feed	ES (1)
Air separator after raw mill [f]	0.01 kg/10^6kg (0.02 lb/10^3 tons) of feed	ES (1)
Raw mill [f]	0.004 kg/10^6kg (0.008 lb/10^3 tons) of feed	ES (1)
Feed to finish mill [f]	0.004 kg/10^6kg (0.008 lb/10^3 tons) of feed	ES(1)
Air separator after finish mill [f]	0.005 kg/10^6kg (0.01 lb/10^3 tons) of feed	ES (1)
Wet process		
Kiln [g]	0.005 kg/10^6kg (0.01 lb/10^3 tons) of feed	ES (2)
Clinker cooler [g]	0.02 kg/10^6kg (0.03 lb/10^3 tons) of feed	ES (1)
Clinker cooler [h]	0.1 kg/10^6kg (0.2 lb/10^3 tons) of feed	ES(1)
Clinker cooler [f]	0.0002 kg/10^6kg (0.0004 lb/10^3 tons) of feed	OES, SSMS (1)
Air separator after finish mill [f]	0.00005 kg/10^6kg (0.0001 lb/10^3 tons) of feed	OES, SSMS (1)

[a] Emissions are uncontrolled unless otherwise specified.

[b] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.

[c] Average particle size of particulate matter is 0.3 micron. [1]

[d] Mean particle size of dust).5 micron. [1]

[e] Mean particle size of particulate matter is 0.7 micron. [1]

[f] Exit from baghouse.

[g] Exit from electrostatic precipitator.

[h] Exit from two baghouses in parallel.

Table 6-2. EMISSION FACTORS FOR MANGANESE FROM FUEL COMBUSTION, COAL

Source	Manganese content, ppm	Emission factor	Emission factor symbol [a]
Power plant study			
South Carolina [b]	— [d]	0.0002 (0.0002 to 0.0003 kg/10^3 kg) 0.0004 (0.0003 to 0.0005 lb/ton)	EST (6)
Michigan [b]	5	0.0002 to 0.005 kg/10^3kg (0.0003 to 0.01 lb/ton)	EST (2)
Illinois [b]	30 to 40	0.0004 to 0.0005 kg/10^3kg (0.0008 to 0.0009 lb/ton)	EST (3)
Average [b]		0.0005 kg/10^3kg (0.001 lb/ton)	EST (11)
Kansas [c]	200	0.001 kg/10^3kg (0.002 lb/ton)	EST (3)
Six-boiler study	— [d]	0.04 kg/10^3kg (0.08 lb/ton)	EST (6)

[a] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.

[b] Exit from electrostatic precipitator.

[c] Exit from limestone wet scrubber.

[d] Not reported.

Table 6-3. EMISSION FACTORS FOR MANGANESE FROM FUEL COMBUSTION, OIL

Source	Manganese content, ppm	Emission factor		Emission factor symbol [a]
		kg/10^3 liters	lb/10^3 gal.	
U. S. crude oil				
Arkansas	0.12	0.0001	0.0009	UK
California	0.138	0.0001	0.001	UK
Colorado	0.208	0.0002	0.001	UK
Kansas	0.013	0.00001	0.00009	UK
Montana	0.005	0.000004	0.00004	UK
New Mexico	0.021	0.00002	0.0001	UK
Oklahoma	0.030	0.00003	0.0002	UK
Texas	0.029	0.00003	0.0002	UK
Utah	1.45	0.001	0.01	UK
Wyoming	0.044	0.00004	0.0003	UK
U. S. crude oil, average	0.21	0.0002	0.001	UK
U. S. residual fuel oils, average	0.16	0.0002	0.001	UK
Residential units (distillate)	— [b]	0.00001 to 0.00004	0.0001 to 0.0003	EST (2)
Commercial units (residential No. 4)	— [b]	0.00002 to 0.00004	0.0002 to 0.0003	EST (2)
Commercial units (residential No. 5)	— [b]	0.00005 to 0.00007	0.0004 to 0.0006	EST(2)
Commercial units (residential No. 6)	— [b,c]	0.00005 to 0.00006	0.0004 to 0.0005	EST (2)

[a] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.

[b] Not reported.

[c] Particle size range for particulate collected with a cascade impactor was 25 percent by weight less than 0.21 micron and 80 percent less than 7.4 microns. Mass median particle size was approximately 1.2 microns.

Table 6-4. EMISSION FACTORS FOR MANGANESE FROM WASTE INCINERATION

Source [a]	Emission factor, kg/10^3kg (lb/ton) of waste burned	Emission factor symbol [b]
Sewage sludge incinerators		
Multiple hearth [c]	0.0005 (0.001) [f]	OES (4)
Fluidized bed [c]	0.0003 (0.0005) [g]	OES (3)
Solid waste incinerator [d]	0.02 (0.03)	EST(1)
Solid waste incinerator [e]	0.004 (0.007)	EST (1)

[a] In this table, all sources are controlled.

[b] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.

[c] Exit from wet scrubber.

[d] Inlet to electrostatic precipitator (could be used as an uncontrolled emission factor).

[e] Exit from electrostatic precipitator.

[f] Range, 0.001 to 0.003 kg/10^3kg (0.002 to 0.006 lb/ton).

[g] Range, 0.0002 to 0.0004 kg/10^3kg (0.0003 to 0.0007 lb/ton).

7. MERCURY

MINING [1]

Cinnabar (HgS) is the main source of mercury. This ore is mined by both open-pit and underground methods. For open-pit operations, emissions of mercury result from dust generated to the ambient air by drilling, blasting, handling, and ore removal. For underground operations, emissions (particulate form) are carried out of the mine by forced ventilation in which all units discharge directly to the atmosphere. The emission factor given in Table 7-1 is based on information obtained from mine operators.

ORE PROCESSING [1-4]

Two basic types of processes are used to recover elemental mercury from the ore. In one process, crushed cinnabar is placed in a retort (816 to 982°C). Mercury is volatilized, and air is allowed to enter the retort to convert sulfur to sulfur dioxide. The vapor is condensed, and mercury is obtained from the condenser. Emissions result from mercury (gaseous and particulate form) in the gas stream discharged from the condenser and from mercury remaining in the calcine. No emission factor is available at present for this process.

The second process emits more mercury than the retort method. The process begins with crushed cinnabar ore (1.75 to 3 kilograms of mercury per 1000 kilograms of ore) being fed to a fired rotary kiln (593 to 760°C). The resultant vapor is vented through a cyclone (sometimes more than one) and condensers before exiting through the stack at temperatures between 32 and 43°C (gaseous and particulate mercury). The mercury is extracted from the condensers by a process called "hoeing" (at atmospheric temperature). A fan usually draws the vapors from the "hoe table" and vents them directly to the atmosphere. After the hoe table, the residual mercury is placed in retorts, which sometimes exit the mercury vapor by way of a condenser before the stack (19°C). Emissions result from all of the stacks from the processes described above.

Two smelter operations were visited, and an EPA gaseous and particulate mercury train was used to obtain stack samples for the smelter stack and hoeing operations.[2] Also, samples were collected from the retort stacks by an EPA gaseous mercury train. All samples were analyzed for mercury by flameless atomic absorption.[3,4]

The emission factors shown in Table 7-1 are based on analytical results and process weight rate of ore at the plants studied. The values are considered uncontrolled factors since cyclones and condensers are part of the recovery process for mercury. The values obtained from the smelter stack agree with Davis' estimate.[1]

SECONDARY PRODUCTION OF MERCURY [1]

Mercury is recovered from battery scrap, dental amalgams, and various sludges. Emissions result from the furnace and calcine bin and from handling and crushing. Davis[1] estimated the emission factor given in Table 7-1.

PROCESSING AND UTILIZATION OF MERCURY AND ITS COMPOUNDS [1]

Most of the mercury recovered from cinnabar is used as a working fluid in instruments and in the production of chlorine and caustic soda. Mercury is also used in the pulp and paper industry and in paints, agricultural sprays, pharmaceutical products, catalysts, etc.

Instruments [1]

Manufacturers that produce switches and relays, thermometers, thermal systems, and flow measuring equipment usually use mercury as the working fluid in the instruments. Emissions in the production of these various instruments usually occur as a result of breakage and spillage. The emission factor in Table 7-2 is based on estimates obtained from manufacturers of these instruments.

Production of Chlorine and Caustic Soda [1,2,5-10]

About 30 percent of the chlorine produced is produced by the mercury cell process (chlor-alkali). Caustic soda is also produced by this cell. The mercury cell is usually a horizontal trough consisting of a electrolyzer and a denuder. A brine

solution and liquid mercury (cathode) are fed continuously into the electrolyzer where chlorine is formed at the anode (graphite), which hangs above the trough but is in contact with the brine. The chlorine is cooled, dried, and liquefied. The sodium forms an amalgam with the mercury. The amalgam flows to the denuder where it becomes the anode to a short-circuited iron or graphite cathode. Hydrogen, mercury, and sodium hydroxide are all formed after the amalgam reacts with water. Emissions of mercury result from the hydrogen stream, cell end-box vent air, and cell room ventilation air. In some plants, the hydrogen stream is purified and employed in the production of chemicals. In most plants, it is considered to be a waste.[1] Control techniques include condensing the hydrogen stream, condensing and contacting the gas with carbon, packed adsorbent beds, mist eliminators, and gas scrubbing. Mist eliminators have been reported to reduce mercury emission with an efficiency of 93 to 99 percent.[5] Packed adsorbent beds have been reported to be more than 99 percent effective.[5,6] Mercury present in cell end-box vent air and cell room air is usually vented to the atmosphere.

Two chlor-alkali plants using the mercury cell process were visited, and an EPA particulate and gaseous mercury train was used to obtain samples from the hydrogen stream and end-box ventilation system. A gaseous mercury EPA train was employed to obtain samples from the cell room ventilation system. Samples from the hydrogen stream (only 15 to 20 percent of the total stream) were taken from the inlet and outlet of a carbon adsorber unit (average efficiency was 48.5 percent).[7,8] All samples taken were analyzed for mercury by flameless atomic absorption.[2] Emission factors based on these studies are presented in Table 7-2. The values for the hydrogen stream have been increased by 85 percent of the inlet stream since the values reported in References 7 and 8 only represent 15 percent of the total hydrogen stream.

In another study, the hydrogen stream capacity for mercury in a 907-kilogram-of-chlorine-per-day plant was determined based on equilibrium concentration corresponding to various gas temperatures.[9] After plotting the experimental data (based on tracer studies) and applying a least squares fit to the data, the mathematical relationship indicated by Equation 7-1 was obtained.

$$y = 0.2305(10^{-11})\, e^{0.728T} \qquad (7\text{-}1)$$

where:

y = emission factor, kg $Hg/10^3$ kg Cl_2

T = temperature of the hydrogen stream, °K

e = exponential function (2.72)

y = intercept

Actual source test data were also compared with the plot (Figure 7-1), but not enough information was available to obtain a relationship. A material balance for the hydrogen stream exiting a heat exchange is also provided in Reference 7. The balance yields values that are larger (by a factor of ten) than the values in Figure 7-1.

Emission factors based on information obtained from industrial sources, material balances, and other sources is also given in Table 7-2 for comparison.[1,9,10] In using the emission factors for the chlor-alkali industry, it is recommended to first use factors based on source test data.

Paints [1]

Mercurial compounds are added to paints as an antifouling agent (mercuric oxides), as a mildew proofing agent, and as a paint preservative (mercuric sulfide). In the production of paints, the compounds are added in the mixing stages, and emissions are considered negligible.

Pharmaceuticals [1]

In the production of various pharmaceuticals, several mercuric compounds may be used (for example, mercuric cyanide, mercuric bichloride, mercuric iodide, and mercuric oxides). The reactions are usually carried out in closed reactors. Emissions during manufacturing are considered negligible.

Pulp and Paper [1]

Emissions for the production of slimicides and the usage of the slimicides in slurries of cellulose fibers are considered negligible.

Amalgamation [1]

Most metals can be amalgamated with mercury. In this application, mercury is used mainly in chemical manufacturing operations and in electrometallurgy. Emissions were estimated by Davis[1] to be negligible.

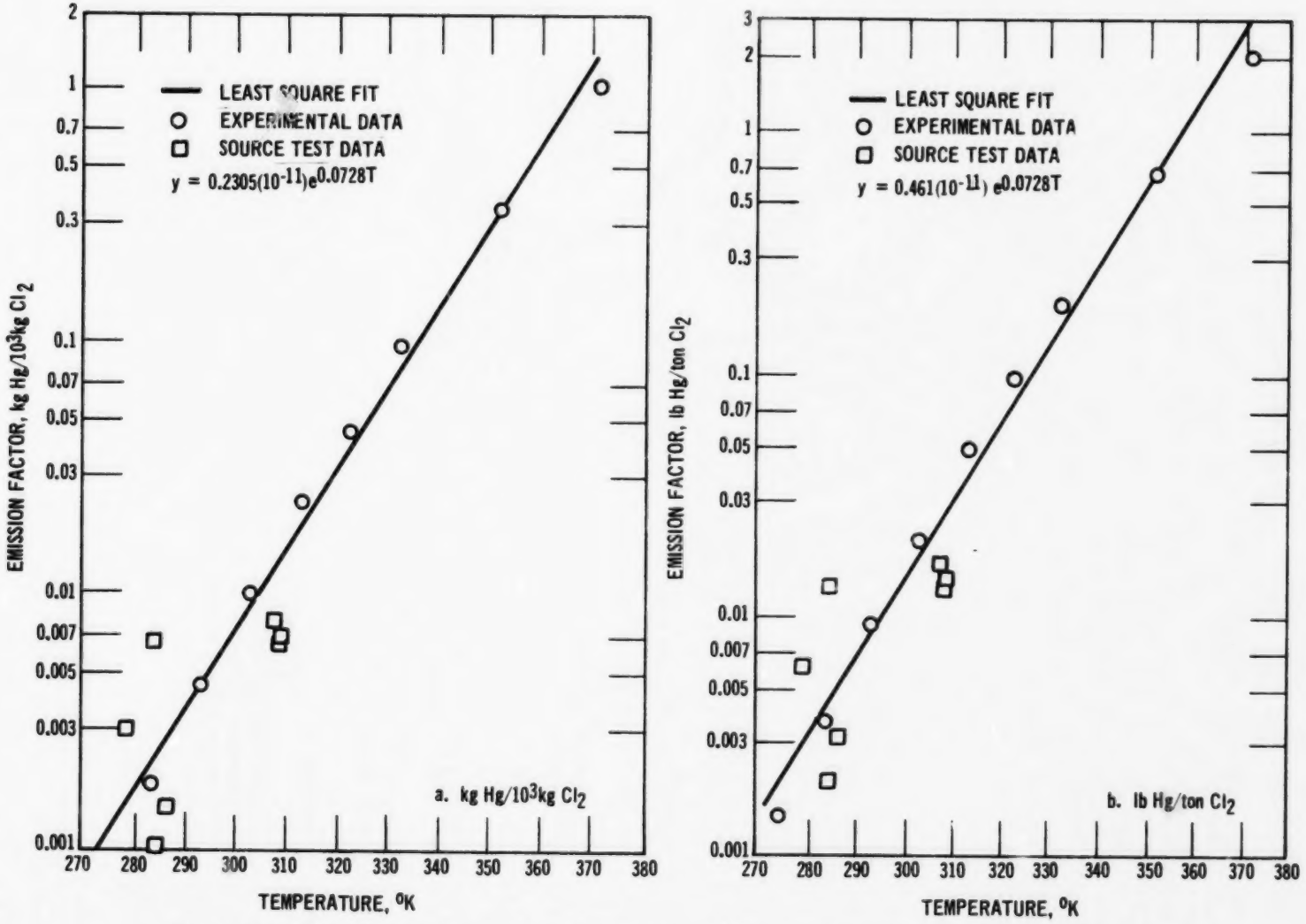

Figure 7-1. Emission factors versus exit temperature of hydrogen stream from a chlor-alkali plant.

Electrical Apparatus [1]

In this category, the largest use of mercury is in the manufacture of batteries employing the mercury cell and alkaline energy cell. Mercury is used in the form of mercuric oxide mixed with graphite and as zinc-mercury alloy. Mercury is also added to fluorescent and high intensity arc discharge lamps. Emissions result from the handling of the mercury or its compounds. The emission factor in Table 7-2 is based on an estimated 4 percent handling loss in which 10 percent of this loss became an atmospheric emission.

Others [1]

No emission factors can be estimated for the use of catalysts (for example, mercuric bichloride and mercuric sulfate) containing mercury that are employed in chemical plants. Likewise, for the production of agricultural sprays (for example, mercuric bichloride and mercuric oxides) no emission information is available.

CONSUMPTIVE USES [1]

Emission factors for the consumptive or nonmanufacturing uses of mercury and its compounds are given in Table 7-3. These uses include paints, agricultural spraying, pharmaceuticals, dental preparations, and general laboratory applications.

Paints [1]

Emissions from paints result from their application. Paints contain from 0.02 to 2.5 percent mercury. Davis [1] estimated the emission factor presented in Table 7-3 based on the amount of mercury present in paints.

Agricultural Spraying [1]

The emission factor presented in Table 7-3 is based on Davis' [1] assumption that about 50 percent of the mercury present in sprays will become an atmospheric emission.

Pharmaceuticals [1]

Emissions from pharmaceuticals result mainly from the application of the antiseptics, skin preparations, and preservatives that contain the mercuric compounds. Davis [1] estimated the emission factor given in Table 7-3.

Dental Preparations [1]

The emissions that result from mercury amalgams used in filling teeth are considered to be handling losses. Handling losses are about 4 percent, with about 1 percent being emitted.

General Laboratory Losses [1]

Emissions from general laboratory use are estimated to be 4 to 13 percent of the mercury used, mainly as a result of handling and experimental losses.

FUEL COMBUSTION

Coal [1,11-15]

A great deal of analytical work has been done on mercury content in coals. In a study involving the determination of mercury present in several coals used for power generation, the average mercury content was 0.2 part per million. [11] The samples came from Pennsylvania, West Virginia, Ohio, Kentucky, Indiana, Missouri, Colorado, Montana, and Arizona. The analytical methods consisted of neutron activation and various atomic absorption techniques. The content of mercury present in the coals ranged from 0.05 to 0.38 part per million; eastern coals contained more mercury than western coals.

In another study, coal samples from two Pennsylvania sites had mercury contents of 0.24 ± 0.02 part per million and 0.31 ± 0.03 part per million. [12] The analytical methods used were the dithizone method, neutron activation, and flameless atomic absorption.

In a third study, fly ash samples from New York power plants were analyzed by atomic absorption. [13] The average amount of mercury present was 0.13 part per million.

In a fourth study, 55 coal samples from Illinois were analyzed. [14] The mercury present ranged from 0.04 to 149 parts per million, with a mean of 0.18 part per million and a mode of 0.10 to 0.12 part per million. Ohio coal and four western coals were also analyzed in this study. The mercury content for the western state coals ranged from 0.02 to 0.09 part per million. The Ohio samples ranged from 0.1 to 0.15 part per million with an average of 0.13 part per million. The analytical method used was neutron activation.

Finally, results are presented for a study in which fly ash samples from two bench scale coal combustors (100 grams per hour and 227 kilograms per hour) and two coal burning power plants were

analyzed by gold-amalgamation flameless atomic absorption spectrophotometry. The flue gas from the 100-gram-per-hour coal combustor was also analyzed for mercury (same analytical method). Mercury was found to be present in all fly ash and flue gas samples. Coals from two different sources (Pennsylvania and Missouri) were utilized in the 100-gram-per-hour combustor. The Pennsylvania coal contained 0.15 ± 0.02 microgram of mercury per gram (12 samples, by flameless atomic absorption) before combustion. The Missouri coal showed a mercury content of 0.24 ± 0.05 microgram of mercury per gram (21 samples, by FAA) before combustion. Percent of total mercury in the fly ash sample ranged from 31 to 37 and from 55 to 66 for the Missouri and Pennsylvania coals, respectively. After analysis of the flue gas samples, the total amount of mercury accounted for ranged from 62 to 96 percent.[15]

For the 227-kilogram-per-hour combustor, a Pennsylvania type coal was utilized for combustion. The mercury content for this coal was 0.019 to 0.04 microgram of mercury per gram of coal (23 samples, by FAA). Total mercury present in the fly ash collected was 12 ± 3 percent. The fly ash samples were collected by a 75 percent efficient cyclone. Therefore, emission factors for this study were increased and decreased, respectively, by 25 percent for the fly ash and flue gas.

The two power plants used Illinois coal with a mercury content of 0.16 ± 0.07 microgram of mercury per gram of coal (32 samples, by FAA). Total mercury contents of the fly ash samples, collected in a mechanical collector at one plant and in an electrostatic precipitator at the other, were 7 and 19 percent, respectively.

The emission factors presented in Table 7-4 (arranged by area rather than individual study) are based on the amount of coal consumed in the United States for 1968 and the average mercury content determined in References 1 and 11 through 14. The emission factors are considered to be the total amount of mercury present in the fly ash and flue gas if no control is applied to the boiler. For comparison, the results for the bench scale combustion and the associated fly ash flue gas analyses[15] have also been converted to emission factors.

Oil [1,16]

All imported residual oils and foreign crude oils, analyzed by neutron activation, contained mercury,[16] the range being 0.005 to 0.30 part per million, with an average of 0.13 part per million for foreign residual fuel oils. The mercury content in foreign crude oils ranged from 0.006 to 0.2 part per million with an average of 0.04 part per million. Most, though not all, U.S. crude oils contained mercury, the range being 0.002 to 0.11 part per million, with an average of 0.06 part per million. Imported low-sulfur fuel oils had the lowest ranges (0.001 to 0.02 part per million) and the lowest average mercury content (0.01 part per million). The emission factors in Table 7-5 are based on the amount of mercury present in the samples, assuming a 100 percent combustion factor and densities of 850 (crude) and 944 (residual) grams per liter for oil.

SOLID WASTE INCINERATION [1,17]

Various products that contain mercury are burned annually. A typical incinerator that burned refuse showed a 0.7 part per million mercury content. The emission factor presented in Table 7-6 is based on this mercury content and on 272,000 kilograms per day of waste burned.

Sewage and sludge also contain mercury. Both are burned at a rate of 1,814,000 kilograms per day in the United States. The emission factor in Table 7-6 is based on an estimated average mercury content of 15 parts per million. Three sludge incinerators were visited, and a gaseous mercury train was employed to collect samples at the scrubber outlets. The samples were analyzed by flameless atomic absorption. Mercury content was found to be extremely low in all samples.

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Table 7-1. EMISSION FACTORS FOR MERCURY FROM MINING, PRIMARY AND SECONDARY SOURCES

Source[a]	Emission factor	Emission factor symbol[b]
Mining	0.005 kg/10^3kg (0.01 lb/ton) of ore mined	Q
Primary ore processing		
Smelter stack	0.16 kg/10^3kg (0.031 lb/ton) of ore processed[c]	FAA (18)
Hoeing operations	0.01 kg/10^3kg (0.02 lb/ton) of ore processed	FAA (3)
Retort operation	0.001 kg/10^3kg (0.002 lb/ton) of ore processed[c]	FAA (3)
Secondary production	20 kg/10^3kg (40 ob/ton) Hg processed	E

[a] All sources are uncontrolled.

[b] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.

[c] Range, 0.09 to 0.22 kg/10^3kg (0.18 to 0.44 lb/ton).

Table 7-2. EMISSION FACTORS FOR PROCESSING AND UTILIZATION OF MERCURY AND ITS COMPOUNDS

Source [a]	Emission factor	Emission factor symbol [b]
Instruments	9 kg/10^3kg (17 lb/ton) of contained Hg	Q
Electrolytic production of chlorine		
Hydrogen stream		
Uncontrolled	0.001 to 0.005 kg/10^3kg (0.002 to 0.01 lb/ton) of Cl_2 produced	FAA (5)
After one carbon adsorber unit	0.0005 kg/10^3kg (0.001 lb/ton) of Cl_2 produced	FAA (2)
End-box ventilation	0.005 kg/10^3kg (0.01 lb/ton) of Cl_2 produced [c]	FAA (6)
Cell room ventilation		
Ridge vent	0.002 kg/10^3kg (0.003 to 0.004 lb/ton) of Cl_2	FAA (4)
Fan ventilation (1 fan)	0.0003 kg/10^3kg (0.0005 lb/ton) of Cl_2 produced	FAA (2)
Loss in hydrogen stream	0.01 kg/10^3kg (0.02 lb/ton) of Cl_2 produced	MB, Q
Loss in ventilation	0.02 kg/10^3kg (0.04 lb/ton) of Cl_2 produced	MB, Q
Comparative data		
Loss in hydrogen stream	0.1 kg/10^3kg (0.2 lb/ton) of Cl_2 produced [d]	UK
End-box ventilation	0.04 kg/10^3kg (0.075 lb/ton) of Cl_2 produced	UK
Cell room ventilation	0.02 kg/10^3kg (0.03 lb/ton) of Cl_2 produced [e]	UK
Paints	Negligible	—
Pharmaceuticals	Negligible	—
Pulp and paper	Negligible	—
Amalgamation	Negligible	—
Electrical apparatus	4 kg/10^3kg (8 lb/ton) of Hg used	E

[a] Uncontrolled unless otherwise specified.
[b] Defined in Table 1-1; number in parentheses indicates number of samples analyzed.
[c] Range, 0.003 to 0.01 kg/10^3kg (0.006 to 0.02 lb/ton).
[d] Range, 0.003 to 7.5 kg/10^3kg (0.006 to 15 lb/ton).
[e] Range, 0.005 to 0.027 kg/10^3kg (0.01 to 0.054 lb/ton).

Table 7-3. EMISSION FACTORS FOR CONSUMPTIVE USES OF MERCURY AND ITS COMPOUNDS

Source	Emission factor	Emission factor symbol[a]
Paint	650 kg/10^3kg (1300 lb/ton) of contained Hg	E
Agricultural spraying	500 kg/10^3kg (1000 lb/ton) of contained Hg	E
Pharmaceuticals	200 kg/10^3kg (400 lb/ton) of Hg applied	E
Dental preparations	10 kg/10^3kg (20 lb/ton) of Hg handled	E
General laboratory handling	40 kg/10^3kg (80 lb/ton) of Hg used	E

[a] Defined in Table 1-1.

Table 7-4. EMISSION FACTORS FROM FUEL COMBUSTION FOR MERCURY, COAL

Source[a]	Mercury content, ppm	Emission factor		Emission factor symbol[b]
		kg/10^6kg	lb/10^3 tons	
Eastern states coals				
Ohio	0.13	0.1	0.3	NA (3)
Belmont County	0.15 ± 0.03	0.15	0.30	NA, FAA, CAA, (32)
Harrison County	0.41 ± 0.06	0.41	0.82	NA, FAA, CAA (28)
Jefferson County	0.24 ± 0.04	0.24	0.48	NA, FAA, CAA (30)
West Virginia				
Kanawha County	0.07 ± 0.02	0.07	0.14	NA, FAA, CAA (27)
Pennsylvania				
Washington County	0.12 ± 0.04	0.12	0.24	NA, FAA, CAA (29)
Pittsburgh bed	0.24 ± 0.02	0.24	0.48	NA, FAA, DM (?)
Lower Kittanning	0.31 ± 0.03	0.31	0.62	NA, FAA, DM (?)
Washington County				
100-g/hr combustor	0.15 ± 0.02	—	—	FAA (12)
Fly ash	0.83 to 0.97 ± 0.13	0.09	0.18	FAA (12)
Flue gas	—	0.06	0.12	FAA (12)
227-kg/hr combustor	0.18 ± 0.04	—	—	FAA (23)
Fly ash	0.22 ± 0.04	0.05	0.09	FAA (17)
Flue gas	—	0.2	0.3	E (17)
Missouri				
Henry County				
100-g/hr combustor	0.24 ± 0.05	—	—	—
Fly ash	0.31 to 0.37 ± 0.06	0.08	0.16	FAA (21)
Flue gas	—	0.16	0.32	E (21)

Table 7-4 (continued) EMISSION FACTORS FROM FUEL COMBUSTION FOR MERCURY, COAL

Source[a]	Mercury content, ppm	Emission factor		Emission factor symbol[b]
		kg/10^6kg	lb/10^3 tons	
Kentucky				
Muhlenberg County	0.19 ± 0.03	0.19	0.38	NA, FAA, CAA (30)
Indiana				
Clay County	0.08 ± 0.02	0.08	0.16	NA,FAA (23)
Illinois	0.18	0.18	0.36	NA (55)
Power plants				
Fly ash	0.10 to 0.26 ± 0.04	0.02	0.04	FAA (32)
Flue gas	—	0.2	0.3	E
New York (fly ash only)	0.13	0.2	0.3	FAA (10)
Western states coals				
Montana	0.08	0.08	0.2	NA (2)
Rosebud County	0.061 ± 0.007	0.061	0.122	NA, FAA, CAA (22)
Colorado	0.02	0.02	0.04	NA (2)
Montrose County	0.05 ± 0.01	0.049	0.098	NA, FAA, CAA (29)
Arizona	0.02	0.02	0.04	NA (1)
Navago County	0.06 ± 0.01	0.06	0.12	NA, FAA, CAA (26)
Utah	0.04	0.04	0.08	NA (1)
Average U.S. coals[c]	0.20	0.20	0.40	NA, FAA, CAA (246)

[a] All sources uncontrolled.

[b] Defined in Table 1-1; number in parentheses indicates number of samples analyzed.

[c] Based on results from Reference 11.

Table 7-5. EMISSION FACTORS FOR MERCURY FROM FUEL COMBUSTION, OIL

Source [a]	Mercury content, ppm	Emission factor		Emission factor symbol [b]
		kg/10^3 liters	lb/10^3 gal.	
Oils				
Imported residual oils				
No. 6 fuel oil, Mexico	0.30	0.0003	0.002	NA (1)
No. 6 fuel oil, Virgin Islands	0.22	0.0002	0.002	NA (1)
No. 6 fuel oil, Trinidad	0.10	0.00009	0.0008	NA (1)
No. 6 fuel oil, Curacao, N.A.	0.13	0.0001	0.001	NA (1)
No. 6 fuel oil, St. Croix, V.I.	0.007	0.000007	0.00006	NA (1)
Bunker "C" fuel oil, Venezuela	0.005	0.000005	0.00004	NA (1)
Average value for imported residual oils	0.13	0.0001	0.001	NA (6)
Imported No. 6 low-sulfur fuel oils				
Virgin Islands	0.007	0.000007	0.00006	NA (2)
Curacao, N.A.	0.02	0.0002	0.0002	NA (1)
Freeport, Bahamas	0.001	0.0000009	0.000008	NA (1)
Average value for imported low-sulfur fuel oils	0.009	0.000008	0.00007	NA (4)
Foreign crude oils				
Neutral Zone-Crude No. 24, Nevada Zone	0.20	0.0002	0.001	NA (1)
Mesa crude oil, Venezuela	0.05	0.00004	0.0004	NA (1)
Monogas crude oil, Venezuela	0.025	0.00002	0.0002	NA (1)

Table 7-5 (continued). EMISSION FACTORS FOR MERCURY FROM FUEL COMBUSTION, OIL

Source [a]	Mercury content, ppm	Emission factor		Emission factor symbol [b]
		kg/10^3 liters	lb/10^3 gal.	
Jobo crude oil, Venezuela	0.016	0.00001	0.0001	NA (1)
Bosean crude oil, Venezuela	0.02	0.00002	0.0001	NA (1)
Kenai Peninsula, Venezuela	0.006	0.000005	0.00004	NA (1)
UMM Tarvo, Libya	0.01	0.000009	0.00007	NA (1)
Gamba, Gabon	0.03	0.00003	0.0002	NA (1)
Tia Juanna, Venezuela	0.05	0.00004	0.0004	NA (1)
Ral Al Khafti, Kuwait	0.09	0.00008	0.0006	NA (1)
Durl, Sumatra	0.04	0.00003	0.0003	NA (1)
Darius, Iran	0.01	0.000009	0.00007	NA (1)
Average value for foreign crude oils	0.05	0.00004	0.0004	NA (12)
U.S. crude oils				
Wesson, Arkansas	0.03	0.00003	0.0002	NA (1)
Midland Farms, Texas	0.08	0.00007	0.0006	NA (1)
East Texas, Texas	0.007	0.000006	0.00005	NA (1)
Yates, Texas	0.06	0.00005	0.0004	NA (1)
Vacuum, New Mexico	0.20	0.0002	0.001	NA (1)
St. Tedesa, Illinois	0.076	0.00006	0.0005	NA (1)
Maysville, Oklahoma	0.002	0.000002	0.00001	NA (1)
Hall-Gurney, Kansas	0.006	0.000005	0.00004	NA (1)
Huntington Beach, California	0.11	0.00009	0.0008	NA (1)
Main Pass, Louisiana	0.06	0.00005	0.0004	NA (1)
Average value for U.S. crude oils	0.05	0.00004	0.0004	NA (10)

[a] All sources uncontrolled.

[b] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.

Table 7-6. EMISSION FACTORS FOR MERCURY FROM SOLID WASTE INCINERATION

Source	Emission factor	Emission factor symbol [a]
Solid waste incineration	0.7 kg/10^6 kg (1 lb/10^3 tons) of refuse burned	E
Sewage sludge incineration Uncontrolled	0.02 kg/10^3 kg (0.03 lb/ton) sewage and sludge burned	E
After wet scrubber	Negligible	FAA (9)

[a] Defined in Table 1-1; number in parentheses indicates number of samples analyzed.

8. NICKEL

MINING AND METALLURGICAL PROCESSING [1]

Open-pit mining is the only type employed in the United States to recover nickel ore. The ore (1.4 percent nickel) is removed by digging or blasting and then shipped to the smelter. The ore is then smelted in electric furnaces and poured into ladles where crushed ferrosilicon is added for the reduction of the ore.

Secondary producers use scrap to prepare a nickel case alloy. This product is sold principally to steel mills. Another product, which is prepared to exact specification, is sold to foundries.

The emission factor presented in Table 8-1 for the mining and metallurgical industry (primary and secondary) is based upon material balance calculations. The value is a controlled emission factor. Control equipment employed includes wet scrubbers, bag filters, and electrostatic precipitators.

PROCESSING OF NICKEL AND ITS COMPOUNDS

Stainless and Heat-resisting Steels [1]

The largest application of nickel is in the production of stainless steels. The nickel contents of stainless steels have an approximate range of 4.5 to 9.3 percent. Emissions of nickel (mainly as nickel oxides) result from the melting process of the various furnaces used in the steel industry. The controlled emission factors (two) given in Table 8-1 are based upon the average of values estimated by manufacturers. Some of the plants employ bag filters as control equipment.

Alloy Steel [1]

About 18.5 percent of all alloy steels produced are nickel alloy steels with an average nickel content of 1.8 percent. Emissions (nickel oxides mainly) result from the melting process in the furnaces employed in the steel industry and from steel or iron scrap, which contain about 1.3 kilograms of nickel per 1000 kilograms of scrap. The emission factors (controlled) presented in Table 8-1 are based on material balances. Emissions are usually controlled by bag filters.

Nickel Alloys [1]

Alloys of this type are morel, sand and casting, nickel-silver, electrical, and electrical resistance alloys. Morel alloys contain more than 50 percent nickel, and nickel silvers (copper-nickel-zinc) have about 15 percent nickel by weight. All alloys have various uses in several different industries. Emissions from the production of these various alloys result mainly from the melting process. The emission factors (four values) given in Table 8-1 are based upon estimates. Bag filters are employed as control devices in the production of nickel alloys, copper base alloys, and electrical alloys. Some control is used in the production of cast iron, but the value in Table 8-1 for cast iron is considered an uncontrolled value.

Electroplating [1]

The process consists of plating nickel with an electrolyte solution. The anode is the nickel and the nickel is deposited on the cathode (some other metal). Emissions from this process are negligible.

Batteries [1]

Nickel-cadmium batteries have several applications in heavy vehicles (diesel and buses) and industry. The process is a sintering operation in which the positive and negative plates consist of sintered carbonyl nickel powder. The active material of the plates is nickel oxide when the battery is charged. Emissions result from handling losses and sintering. Usually no controls are employed in this industry. The emission factor given in Table 8-1 is based upon manufacturers' estimates.

Catalysts [1]

Nickel compounds are used in various industries producing vegetable oils, ammonia, petrochemicals, hydrogen, and many other products. Emissions reported by manufacturers are considered negligible.

CEMENT PLANTS

Cement manufacturing processes are described in Chapter 4. Emissions from both dry and wet process cement plants can result from all of the processes described.

Dry Process [2]

Two plants using the dry processing method were visited, and particulate samples were obtained by the EPA sampling train method. Baghouses were employed as air pollution control equipment at both plants on all processes described. The probes for the sampling train were placed in the stack area after each baghouse. Some of the samples (total catch) were analyzed by emission spectroscopy for trace metals. The emission factors in Table 8-1 were based on percent of nickel present in the sample and the emission factor calculated for total particulates emitted. The final cement from one plant was analyzed, and it also contained nickel (80 micrograms per gram).

Wet Process [3]

Particulate emissions were obtained from the kilns, clinker cooler, and finishing mill of three plants that used the wet process. The same analytical techniques were employed as described in the dry process section except that part of one sample was analyzed by spark source mass spectrograph and optical emission spectrograph. Sampling was done at the exits of the baghouses or electrostatic precipitators employed at the individual plants. Emission factors (Table 8-1) were calculated as described in the section for the dry process.

CONSUMPTIVE USES OF NICKEL AND ITS COMPOUNDS

Nickel and its compounds are used in the pulp and paper, petroleum, and chemical industries. Emissions to the atmosphere are considered negligible.

FUEL COMBUSTION

Coal [1,4,5]

Several studies for trace metal emissions from coal fired boilers have been done. In one study, several boilers using coal from different parts of the United States were studied. Fly ash samples were collected and analyzed by emission spectrometry for nickel and other trace metals. Nickel concentrations ranged from 133 to 690 micrograms per cubic meter. The emission factor given in Table 8-2 is based on the yearly consumption of coal, 75 percent control of particulates, nickel concentration of 133 micrograms per cubic meter, and 9.9 cubic meters per kilogram of coal.[1]

In another study, fly ash samples were collected from five power plants and the samples were analyzed by emission spectrometric methods for trace metals.[4,5] The samples were all collected by an EPA sampling train with the probe of the train placed in the stack after the electrostatic precipitator or wet scrubber control equipment. Nickel was present in all samples, the range being 50 to 290 micrograms per gram. Three coal samples at three of the individual plants were also analyzed, and nickel was again present, the range being 10 to 30 micrograms per gram with an average of 16 micrograms per gram. The emission factors presented in Table 8-2 are based upon the percent of nickel present in the fly ash samples analyzed and emission factors estimated in the studies for particulates, which were based on total particulate catch.

Oil [1,6,7]

According to Davis,[1] nickel content of U.S. crude oils ranged from 1.4 to 64 parts per million with an average of 15 parts per million. Nickel content in imported crude oils ranged from 0.3 to 28.9 parts per million with an average of 10 parts per million. The anaiytical method used to determine trace metals present was not reported. The emission factors given in Table 8-3 for this study are based on the amount of nickel present, assuming a 100 percent combustion factor and a density of 850 grams per liter for crude oil.

In a second study, foreign crude and residual oils from different oil fields were analyzed by flame atomic absorption. All samples analyzed showed nickel to be present. The nickel content in the foreign crude oils averaged about 25.6 parts per million (ranged from 1.8 to 59 parts per million). The foreign crude oils showed an average nickel content of about 36.3 parts per million (ranged from 4 to 61 parts per million).[6] The emission factors for this study (Table 8-3) are based on the amount of nickel found in the oil samples, an assumed 100 percent combustion factor, and densities of 850 (crude) and 944 (residual) grams per liter for oil.

Another study in which residential (distillate fuel) and commerical (residual fuel) oil burning units were studied showed nickel being emitted to the atmosphere.[7] An EPA sampling train was employed to catch particulates. The particulates

were analyzed for trace metals by optical emission spectrometry. The emission factors based on this study (Table 8-3) are lower than the values based on nickel content alone. This would be the case if some of the nickel or nickel compound were in the vapor phase.

Gasoline

Nickel compounds may be present in some gasolines. At present there is not enough information available to give an accurate emission factor.

WASTE INCINERATION [8,9,10]

Sewage sludge and sewage sludge-mixed refuse incinerators will be discussed in this section. Also, an emission factor for waste lubrication oil is provided in Table 8-4.

There are two main types of sewage sludge incinerators: multiple hearth and fluidized bed. Both incinerators have similar designs, with the only major difference being that ash is removed from the bottom of the multiple hearth furnace, but in the fluidized bed all the ash is carried overhead and is removed by a scrubber. Scrubbers (impinjet, inertial jet, and venturi) are a part of the process design of sewage sludge incinerators.

Three sewage sludge incinerators were visited, and particulate samples were obtained by the EPA sampling train method. The samples were analyzed by emission spectroscopy, and nickel was found in all but one of the samples. [8]

One sewage sludge-mixed refuse incinerator was visited and particulate samples were collected using a null balance probe. The samples were analyzed by atomic absorption for nickel.[9]

The emission factors presented in Table 8-4 are based on process conditions and amount of nickel found in the particulate matter analyzed.

Several lubricating oils have also been analyzed by EPA for trace metals. Nickel was present in all oils and the emission factors ranged from 0.002 to 0.03 kilogram per 1000 liters of waste crankcase oil, with an average value of 0.008 kilograms of nickel oxides per 1000 liters of waste crankcase oil.[10]

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Table 8-1. EMISSION FACTORS FOR NICKEL FROM INDUSTRIAL SOURCES

Source[a]	Emission factor	Emission factor symbol[b]
Mining and metallurgical	9 kg/10^3kg (17 lb/ton) of Ni produced	MB
Processing of nickel and its compounds		
Stainless steel	5 kg/10^3kg (10 lb/ton) of Ni charged or 0.3 kg/10^3 kg (0.6 lb/ton) of stainless steel produced	Q
Nickel alloy steels[c]	5 kg/10^3kg (10 lb/ton) of Ni charged	MB
Iron and steel scrap	0.0008 kg/10^3 kg (0.0015 lb/ton) of steel and iron	MB
Nickel alloys (other)[d]	1 kg/10^3kg (2 lb/ton) of Ni charged	E
Copper base alloys[d]	1 kg/10^3kg (2 lb/ton) of Ni charged	E
Electrical alloys[d]	1 kg/10^3kg (2 lb/ton) of Ni charged	E
Cast iron	10 kg/10^3kg (20 lb/ton) of Ni charged	E
Electroplating	Negligible	—
Batteries	4 kg/10^3kg (8 lb/ton) of Ni processed	Q
Catalysts	Negligible	—
Cement plants		
Dry process		
Kiln[d]	0.2 kg/10^6kg (0.3 lb/10^3 tons) of feed	ES (1)
Feed to raw mill[d]	0.005 kg/10^6kg (0.01 lb/10^3 tons) of feed	ES (1)
Air separator after raw mill[d]	0.0005 kg/10^6kg (0.001 lb/10^3 tons) of feed	ES (1)
Raw mill[d]	0.0003 kg/10^6kg (0.0006 lb/10^3 tons) of feed	ES (1)
Air separator after finish mill[d]	0.002 kg/10^6kg (0.003 lb/10^3 tons) of feed	ES (1)
Feed to finish mill[d]	0.005 kg/10^6kg (0.01 lb/10^3 tons) of feed	ES (1)

Table 8-1 (continued). EMISSION FACTORS FOR NICKEL FROM INDUSTRIAL SOURCES

Source [a]	Emission factor	Emission factor symbol [b]
Wet process		
Kiln [e] (2 different plants)	0.1 to 1 kg/10^6kg (0.2 to 2 lb/10^3 tons) of feed	ES (2)
Clinker cooler [d]	0.002 kg/10^6kg (0.004 lb/10^3 tons) of feed	SSMS, OES (2)
Clinker cooler [e]	0.05 kg/10^6kg (0.1 lb/10^3 tons) of feed	ES (2)
Clinker cooler [f]	0.1 kg/10^6kg (0.2 lb/10^3 tons) of feed	ES (2)
Finishing mill after air separator [d]	0.002 kg/10^6kg (0.004 lb/10^3 tons) of feed	SSMS, OES (1)

[a] Uncontrolled unless otherwise specified.

[b] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.

[c] Considered controlled.

[d] Exit from baghouse.

[e] Exit from electrostatic precipitator.

[f] Exit from two baghouses (in parallel).

Table 8-2. EMISSION FACTORS FOR NICKEL FROM FUEL COMBUSTION, COAL

Source [a]	Nickel content, ppm	Emission factor		Emission factor symbol [b]
		kg/10^3kg	lb/ton	
Coal-fired boilers	-- [e]	0.0002	0.003	EST (6)
Power plant study				
South Carolina [c]	-- [e]	0.0003 (0.0002 to 0.0005)	0.0007 (0.0004 to 0.0009)	EST (6)
Michigan [c]	10	0.0003 (0.0002 to 0.0005)	0.0006 (0.0003 to 0.0009)	EST (2)
Illinois [c]	10 to 20	0.0002	0.0003	EST (2)
Average [c]	12	0.0003	0.0006	EST (10)
Kansas [d]	30	0.0003 (0.0002 to 0.0005)	0.0006 (0.0003 to 0.0009)	EST (2)

[a] Uncontrolled unless otherwise specified.

[b] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.

[c] Exit from an electrostatic precipitator.

[d] Exit from wet scrubber.

[e] Not reported.

Table 8-3. EMISSION FACTORS FOR NICKEL FROM FUEL COMBUSTION: OIL

Source [a]	Nickel content, ppm	Emission factor		Emission factor symbol [b]
		kg/10^3 liters	lb/10^3 gal.	
U.S. crude oils				
Texas	2.4 (1.4 to 4.3)	0.002 (0.001 to 0.004)	0.02 (0.01 to 0.03)	UK (3)
Louisiana	2.1	0.002	0.01	UK
Kansas	6.3	0.005	0.04	UK
Wyoming	2.7	0.002	0.02	UK
California	64	0.05	0.5	UK
Alaska	11.3	0.01	0.08	UK
Average for U.S. crude oils	15 (1.4 to 64)	0.01	0.1	UK
Average for imported crude oils	10 (0.3 to 28.9)	0.009	0.07	UK
Foreign crude oils				
Monogas crude, Venezuela	44.1	0.04	0.3	CAA (1)
Crude oil, Venezuela	7	0.006	0.05	CAA (1)
Nigerian crude oil	8.8	0.007	0.06	CAA (1)
Jobo crude, Puerto Ordaz, Venezuela	59	0.05	0.4	CAA (1)
Aguasay crude oil, Venezuela	1.8	0.002	0.01	CAA (1)
Average for foreign crude oils	25.6	0.02	0.2	CAA (5)
Foreign residual oils				
No. 6 fuel oil, Virgin Islands	31.8 to 33.8	0.03	0.3	CAA (2)

Table 8-3 (continued. EMISSION FACTORS FOR NICKEL FROM FUEL COMBUSTION, OIL

Source [a]	Nickel content, ppm	Emission factor		Emission factor symbol [b]
		kg/10^3 liters	lb/10^3 gal.	
No. 6 fuel oil, Venezuela	40.5 (4 to 61.2)	0.04 (0.004 to 0.06)	0.3 (0.03 to 0.5)	CAA (7)
No. 6 fuel oil, Aruba, N.A.	35.2	0.03	0.3	CAA (1)
No. 6 fuel oil, St. Croix, V.I.	15.5	0.01	0.1	CAA (1)
No. 6 fuel oil, El Patito, Venezuela	59.7	0.06	0.5	CAA (1)
No. 6 fuel oil, Puerto La Auz Venezuela	48	0.05	0.4	CAA (1)
No. 6 fuel oil, Spain	17.9	0.02	0.1	CAA (1)
No. 6 fuel oil, Trinidad	29 to 35	0.03	0.2 to 0.3	CAA (2)
No. 6 fuel oil, Canada	22.7	0.02	0.2	CAA (1)
Average for foreign fuel oils	36.3 (4 to 61.2)	0.03 (0.004 to 0.06)	0.3 (0.03 to 0.5)	CAA (17)
U.S. boilers Residential units (distillate)	– [d]	0.00005 to 0.00006	0.0004 to 0.0005	EST (2)
Commercial units (residual No. 6)	48.5	0.01	0.08	EST (1)
Commercial units (residual No. 5)	31	0.007	0.06	EST (1)
Commercial units (residual No. 4)	18	0.006	0.05	EST (1)

[a] Uncontrolled unless otherwise specified.
[b] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.
[c] Particle size distribution (particulate collected with a cascade impactor): 25 percent (by weight) less than 0.21 micron, – 80 percent less than 7.4 microns, mass mean particle size approximately 1.2 microns.
[d] Not reported.

Table 8-4. EMISSION FACTORS FOR NICKEL FROM WASTE INCINERATION

Source [a]	Emission factor	Emission factor symbol [b]
Sewage sludge incinerators		
Multiple hearth [c]	0.002 kg/10^3kg (0.003 lb/ton) of solid waste incinerated [d]	OES (4)
Fluidized bed [c]	0.0002 kg/10^3kg (0.0003 lb/ton) of solid waste incinerated [e]	OES (2)
Municipal incinerator		
Refuse only [c]	0.002 kg/10^3kg (0.003 lb/ton) of solid waste incinerated	CAA (3)
Refuse and sludge [c]	0.003 kg/10^3kg (0.005 lb/ton) of solid waste incinerated	CAA (3)
Lubricating oil	0.008 kg/10^3 liters (0.07 lb/10^3 gal.) of lubricating oil [f]	UK

[a] In this table, all sources except lubricating oil are controlled.

[b] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.

[c] Emission from wet scrubber.

[d] Range, 0.0003 to 0.004 kg/10^3kg (0.0006 to 0.008 lb/ton).

[e] Range, 0.0001 to 0.0002 kg/10^3kg (0.0002 to 0.0003 lb/ton).

[f] Emission factor for nickel oxides.

9. VANADIUM

MINING AND PROCESSING [1,2]

Vanadium occurs in many ores. It is found in such minerals as patronite, bravoite, sulvanite, davidite, and roscoelite. Vanadium is also present in uranium-bearing sandstones, iron ores, phosphate rock, and titaniferous magnetite ores. The concentrations of vanadium in the ores range from 0.01 to 25 percent. Vanadium is mainly recovered from uranium and vanadium ores, and from phosphate rock. The mining operations consist of surface and underground ore recovery. For underground operations, the process consists of drilling, blasting, conveyance of ore to the surface, and transportation to the mill. Surface mining mainly consists of removing the overburden by blasting and then transporting the ore to the mill area.[1] Emissions result from all processes described above. No controls are known by this author to be employed.

In processing for the recovery of vanadium pentoxide, the ores are first dry ground, mixed with lime and salt, and roasted. Sodium vanadate is produced from the roaster and is bleached with water, acid, or a basic solution. The solution is precipitated (sodium polyvanadate is produced) and redissolved, thus causing the precipitation of ammonium acetavanadate to take place. This product is fused to yield vanadium pentoxide. The product is of technical grade and contains 86 percent vanadium pentoxide (6 to 10 percent sodium oxide). Emissions probably result from the roasting operation and handling. The metal has a low vaporization temperature and recovery rates have been estimated at between 30 and 75 percent of the metal present initially.[2] The emission factor in Table 9-1 is based on information obtained from the mining and milling industry.

METALLURGICAL PROCESSING

Ferrovanadium [1,3]

The technical grade oxide, vanadium ore, or slag is further reduced to ferrovanadium, which is mainly used by the steel industry. The reduction is carried out by carbon, ferrosilicon, or aluminum. Reduction by carbon is done by an electric reduction furnace or a vacuum furnace in which charges are placed in the top of the furnace and the molten product removed at the bottom. A vacuum furnace product of ferrovanadium has been reported to contain about 85 percent vanadium, 12 percent carbon, and 2 percent iron.[3]

Two processes are available for the production of ferrovanadium by ferrosilicon reduction. In one process about 90 percent grade ferrosilicon is mixed with lime, vanadium pentoxide, and fluorspar. The mixture is smelted in an electric furnace lined with magnesite. The product contains about 30 percent vanadium, iron, and undesirable amounts of silicon. The silicon concentration is reduced by adding more vanadium pentoxide and lime. This step enables the silicon to go into the slag phase, and the slag is recycled to the first step of the process.

The second process in which silicon is employed involves the reaction between vanadium bearing slag, silica, carbonaceous reducer, and a flux inside a submerged-arc electric furnace. The alloy product, vanadium silicide alloy, is refined with vanadium oxide until the concentration of silicon present in the alloy is less than 20 percent. This alloy is reacted with molten vanadiferous slag and lime to yield a ferrovanadium alloy called Solvan (28 percent vanadium, 11 percent other metals, and the rest iron).

The reduction by aluminum can also be done by two processes. In the first, the reactants of vanadium pentoxide, aluminum, iron scrap, and a flux are placed in an electric arc furnace. The product from the reaction contains about 80 percent vanadium. In the second process, called the thermite reaction, vanadium and iron oxide are both reduced by aluminum granules. The reaction is initiated by a barium peroxide-aluminum ignition charge.

In each of the reduction processes discussed, vanadium pentoxide is melted first before alloying is done. The actual reduction process in the furnace consists of the pentoxide going to tetroxide, trioxide, oxide, and vandium metal.

Emissions from the above processes are from the furnaces and from handling the molten

material. The emission factor for electric furnaces in Table 9-1 is based on uncontrolled emissions, stack samples, and chemical analysis of the particulates from the stack samples. The emission factor for handling was estimated by Davis.[1]

Vanadium Metal [1,2]

In one process used to obtain vanadium metal, vanadium pentoxide is reduced by calcium (iodine is also added). The reactants are all placed in a sealed vessel, and calcium iodide, which serves as a flux and thermal booster, is formed. The product is about 99.5 percent pure vanadium. Another process, called the alumino-thermic process, produces 99 percent pure vanadium and employs powdered vanadium pentoxide, which reacts with aluminum in a sealed vessel. The molten alloy of vanadium and aluminum settles to the bottom of the vessel from a fused aluminum oxide slag. The alloy is purified by crushing and melting by both heat and an electron beam.

Vanadium metal can be further purified by iodide refining, electrolytic refining in a fused salt, or electrotransport. In the iodide refining process, the iodide is reacted with vanadium metal to form vanadium diodide, which is in vapor form. The vanadium diodide is decomposed and deposited on a hot filament. The electrolytic process involves the cathodic deposition of vanadium from an electrolyte in solution. Electrotransport consists of a high-density current being passed through a vanadium rod (heating to 1700 to 1850°C) with migration of carbon, oxygen, and nitrogen atoms at the negative end of the rod. Emissions result from the handling of the molten mass, from crushing, and possibly from the electron beam melting employed in the alumino-thermic process. Most reactions are inside sealed vessels that reduce emissions. Not enough data are available to obtain a reasonable emission factor for any process discussed in this section.

Vanadium Carbide [1]

Vanadium carbide is sometimes used as a replacement for ferrovanadium in the steel industry. The carbide is produced by heating powdered vanadium metal, a hybride, and carbon in a vacuum furnace (2000°C). Emissions can result if a low carbon product is desired and low temperatures are not employed in the heating. No emission factor can be determined for this process at present.

STEEL PRODUCTION [1]

Emissions of vanadium from the steel industry are mainly due to impure vanadium or the pentoxide being present in the iron ore. The amount of vanadium present in the ore ranges from 0.01 to 0.1 percent. This range was estimated by people contacted in the steel industry. Emissions from alloying vanadium with steel are of less importance in considering air pollution. The vanadium is added to the melt at the end of the refining process or after the steel is in the ladle.

Blast Furnace [1,4]

In the production of steel, the first step involves the removal of impurities from iron ore in a blast furnace. Coke and limestone are also charged with the iron ore in the furnace. Large amounts of particulates are produced in this process.[4] The gas stream is usually cleaned with an estimated efficiency of 97 percent.[1] The emission factor in Table 9-1 is based on an estimated vanadium content of 0.03 percent in the iron ore (with 5 percent being lost). For further purification of the pig iron into steel an open hearth, a basic oxygen, or an electric furnace is used.

Open-hearth Furnace [1,4,5]

In the open hearth furnace, steel is made from a mixture of scrap (which also contains vanadium) and pig iron (about 55 percent pure) in a shallow basin or hearth. The process consists of several stages: tap to start, charging, meltdown (1650°C), hot-metal addition, ore and lime boil, working, tapping, and delay. Emissions of metal oxides are continuous and varied during the operational cycles described. For an uncontrolled process, the particulate emitted is 6 (no oxygen lance) and 11 (oxygen lance) kilograms per 1000 kilograms of steel produced.[4] The amount of vanadium emitted in the particulate matter is about 0.05 percent.[1,5] The emission factor presented in Table 9-1 is based on this value.

Basic Oxygen Furnace [1,6]

The furnace consists of a refractory-lined cylindrical vessel mounted on trunions. The charge consists of steel scrap, molten pig iron, and sometimes alloying materials. The furnace is charged in the vertical position, and oxygen is supplied, causing agitation and mixing of the molten mass. Emissions result from the molten mass and are usually controlled by scrubbers, cyclones, or a combination of control equipment. The emission factor presented in Table 9-1 is based on an emission spectrographic study done on a steel plant. A sample for particulates was taken by an EPA sampling train and then was analyzed for trace metals. The probe was placed in the stack of the basic oxygen furnace after two venturi

scrubbers. The amount of vanadium present was 0.014 percent of the total particulate emitted (which was determined to be 0.00675 kilogram per 1000 kilograms of steel). The emission factor is small compared to Davis' value,[1] which was based on a 0.02 percent concentration of vanadium in the particulate (23 kilograms of particulate per 1000 kilograms steel for uncontrolled value).

Electric Furnace [1]

Electric furnaces are refractory-lined cylindrical vessels with carbon electrodes passing through the top of the furnace. Emissions from this furnace result from charging, refining, and pouring of the molten mass. Davis[1] felt that emissions are negligible for vanadium in electric furnaces.

CAST IRON PRODUCTION [1]

The cupola is the method most widely used for the production of cast iron. Emissions occur mainly from the melting of the iron ore. The amount of vanadium present in particulates, according to industry sources, is about 0.001 percent. The emission factor in Table 9-1 is based on this value.

CEMENT PLANTS

Cement manufacturing processes are described in Chapter 4. Vanadium emissions from cement plants are due to the presence of vanadium as an impurity in one of the initial chemicals used to produce cement. Emissions from both dry and wet process cement plants can result from all of the processes described.

Dry Process [7]

Two plants using the dry process were visited, and particulate samples were obtained by the EPA sampling train method. Baghouses at both plants were employed as air pollution control equipment. The probes for the sampling train were placed in the stack area after each baghouse. Stacks from which samples were taken included the kilns (at one plant only), raw mill grinding system, and finish mill grinding system. Some of the samples (total catch) were analyzed by emission spectroscopy for trace metals. The emission factors (Table 9-1) were based on percent of vanadium present in the sample and the emission factor calculated for total particulates.

Wet Process [8]

Particulate emissions were obtained from the kilns, clinker cooler, and finishing mill of three wet process plants. The same analytical techniques were employed as described in the dry process section, except that part of one sample was analyzed by spark source mass spectrography and optical emission spectrography. Sampling was done at the exits of the baghouses or electrostatic precipitators employed at the individual plants. Basis for emission factor estimates (Table 9-1) is also as described in the section for the dry process.

PROCESSING OF VANADIUM AND ITS COMPOUNDS

Nonferrous Alloys [1]

Vanadium metal is also employed as an alloying agent with nonferrous metals (aluminum and titanium mainly) to control grain size, thermal expansion, and electrical resistivity. The emission factor in Table 9-1 is based on two industrial sources.

Catalysts [1]

Catalyst manufacturers use vanadium pentoxide or ammonium metavanadate as starting reactants for the production of catalysts. In one process, vanadic acid is produced and caustic potash, dilute sulfuric acid, and water are added to the acid. The mass is dried and placed in a calcining furnace (at 800°C). The product is cooled and sieved. The major source of emissions is the furnace, and the emission factor in Table 9-1 is based on manufacturers' estimates.

Ceramics and Glass [1]

The use of vanadium in glass and ceramics is for the production of a yellow stain for coloring pottery and glass. Emissions of vanadium in this industry are considered negligible.

Miscellaneous [1]

Vanadium is also alloyed with magnetic alloys and steel (already discussed). Compounds of vanadium are placed in paint oil as a drying agent. Vanadium chloride is used in toning silver bromide in the development of color film.

In alloying, the vanadium is usually added in the ladle. Emissions therefore are at a minimum. For paint oils, the vanadium compounds can be added in the paint-mixing process or during the cooling period (230 to 316°C). Emissions result mainly during the cooling period. Vanadium chloride, used in color film toning, is produced by heating vanadium pentoxide with sulfur monochloride to produce vanadium trichloride. The trichloride is reduced by a nitrogen stream (at 800°C) to produce vanadium chloride. Emissions result mainly from this stream. Emission factors

for all of the processes described above are based on losses estimated by manufacturers to range from less than 0.25 to 5 percent.

FUEL COMBUSTION

Coal [1,9,10]

Fly ash samples from five power plants were analyzed by emission spectrometric methods to determine trace metals present.[9,10] The samples were all taken by an EPA sampling train, with the probe of the train placed in the stack after the electrostatic precipitator or wet scrubber control equipment. Vanadium was present in all samples analyzed. The values of vanadium present ranged from 70 to 180 micrograms per gram (weight fraction) with an average value of 116 micrograms per gram. The emission factors presented in Table 9-2 are based upon the percent of vanadium present in the fly ash sample analyzed and emission factors estimated in the studies for particulates.

The last value is based on the amount of vanadium present in the coal initially. The range of vanadium present was 16 to 35 parts per million with an average of 22.5 parts per million. It was assumed that 65 percent of the vanadium went with the bottom ash.[1]

Oil [1,11]

Analyses of over 400 samples of crude and residual oils from major oil companies and utilities on the east coast of the United States were obtained.[1] The results showed vanadium to be present in all samples. In crude oils (foreign and domestic), the vanadium present ranged from less than 1 to 1000 parts per million. The residual fuel oils showed higher ranges (30 to 90 percent) than the crude oils. Crude oils from the United States showed a vanadium range of 0.1 to 78 parts per million, with an average of 19.5 parts per million. Residual oils of the United States average 30 parts per million of vanadium, and the range was not reported. Crude oils from Venezula ranged from less than 1 to 1400 parts per million of vanadium, with an average between 116 and 356 parts per million. South American residual and crude oils have an average vanadium content of 280 parts per million. Crude oils from the Middle East contained from 3 to 114 parts per million vanadium, with an average of 43 parts per million. Residual oils from the same area have an average content of 50 parts per million vanadium. Emission factors based on these values are presented in Table 9-3.

Another study in which residential (distillate fuel) and commerical (residual fuel) oil burning units were studied showed vanadium being emitted to the atmosphere.[11] An EPA sampling train was employed to catch particulates. The particulates were analyzed for trace metals by optical emission spectrometry. The emission factors are given in Table 9-3. The emission factors are lower than the values obtained based on vanadium content alone.

SOLID WASTE INCINERATION [12]

Incineration of waste material that contains vanadium is another source of emissions for this trace metal. However, there is limited information, and the emission factors presented in Table 9-4 are based on stack analysis of only one incinerator. The analytical procedure employed to analyze for vanadium was emission spectrography.

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Table 9-1. EMISSION FACTORS FOR VANADIUM FROM INDUSTRIAL SOURCES

Source [a]	Emission factor	Emission factor symbol [b]
Mining and processing	13 kg/10^3k (25 lb/ton) of vanadium processed	Q
Metallurgical processing		
Ferrovanadium, electric furnaces [c]	25 kg/10^3kg (50 lb/ton) of vanadium processed	UK
Handling losses	5 kg/10^3kg (10 lb/ton) of vanadium processed	E
Steel production		
Blast furnace	0.02 kg/10^3kg (0.03 lb/ton) of pig iron produced	E
Open-hearth furnace		
No oxygen lance	0.003 kg/10^3kg (0.006 lb/ton) of steel produced	OES (1)
Oxygen lance	0.006 kg/10^3kg (0.01 lb/ton) of steel produced	OES (1)
Basic oxygen furnace [d]	0.001 kg/10^6kg (0.002 lb/ton) of steel produced	OES (1)
Basic oxygen furnace	0.005 kg/10^3kg (0.009 lb/ton) of steel produced	E
Electric furnace	Negligible	—
Cast iron production	0.1 kg/10^6kg (0.2 lb/10^3 ton) of charge	Q
Cement plants		
Dry process (for all processes)	— [h]	ES (6)
Wet process		
Kiln (average of two) [e]	0.05 kg/10^6kg (0.1 lb/10^3 ton) of feed	ES (2)
Clinker cooler [f]	0.0003 kg/10^6kg (0.0005 lb/10^3ton) of feed	OES, SSMS (1)
Clinker cooler [e]	0.01 kg/10^6kg (0.02 lb/10^3 ton) of feed	ES (1)
Clinker cooler [g]	— [h]	ES (1)
Finishing mill after air separator [f]	0.0001 kg/10^6kg (0.0002 lb/10^3 ton) of feed	OES, SSMS (1)
Processing of vanadium and its compounds		
Nonferrous alloys	6 kg/10^3kg (12 lb/ton) of vanadium processed	Q
Catalysts	10 kg/10^3kg (20 lb/ton) of vanadium processed	Q
Glass and ceramics	Negligible	—
Miscellaneous (steel alloying, magnetic alloys, paint oils, color film)	5 kg/10^3kg (10 lb/ton) of vanadium processed	Q

[a] Uncontrolled unless otherwise specified.
[b] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.
[c] Particle size, 0.1 to 1 micron.[1]
[d] Exit from two venturi scrubbers.
[e] Exit from electrostatic precipitator.
[f] Exit from baghouse.
[g] Exit from two baghouse collectors (in parallel).
[h] Emission below detection limit of analytical technique.

Table 9-2. EMISSION FACTORS FOR VANADIUM FROM FUEL COMBUSTION, COAL

Source[a]	Vandium content, ppm	Emission factor		Emission factor symbol[b]
		kg/10^3kg	lb/ton	
Illinois[c]	20	0.0003 (0.0003 to 0.0004)	0.0006 (0.0005 to 0.0007)	EST (3)
South Carolina[c]	—[e]	0.0002 (0.0002 to 0.0003)	0.0004 (0.0003 to 0.0006)	EST (6)
Michigan[c]	10	0.0003 (0.0002 to 0.0003)	0.0005 (0.0003 to 0.0006)	EST (2)
Average[c]	15	0.0003	0.0006	EST (11)
Kansas[d]	10 to 20	0.002	0.003 (0.003 to 0.004)	EST (2)
Based on vanadium content in coal	22.5	15	30	UK

[a] Controlled unless otherwise specified.

[b] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.

[c] Exit from electrostatic precipitator.

[d] Exit from limestone wet scrubber.

[e] Not reported.

Table 9-3. EMISSION FACTORS FOR VANADIUM FROM FUEL COMBUSTION, OIL

Source[a]	Vanadium content, ppm	Emission factor		Emission factor symbol[b]
		kg/10^3 liters	lb/10^3 gal.	
Crude oils, U.S.				
Arkansas	9.3	0.008	0.07	UK
California	50.0	0.04	0.4	UK
Colorado	00.44	0.0004	0.003	UK
Kansas	15.1	0.01	0.1	UK
Louisiana	0.5	0.0004	0.004	UK
Montana	78	0.07	0.6	UK
New Mexico	0.1	0.00009	0.0007	UK
Oklahoma	4.0	0.003	0.03	UK
Texas	2.6	0.002	0.02	UK
Utah	4.6	0.004	0.03	UK
Wyoming	49.7	0.04	0.4	UK
Average for U.S. crude oils	19.5	0.02	0.1	UK
Average, residual oil - United States	30	0.03	0.2	UK
Foreign crude and residual oil				
Average, crude oil - Western Venezuela	356	0.3	3	UK
Average, crude oils - Eastern Venezuela	116	0.1	0.8	UK
Average, residual oil - Venezuela	280	0.3	2	UK
Average, residual oil - Middle East	50	0.05	0.4	UK
U.S. boilers				
Residual units (distillate)	—[d]	0.000008	0.00007	ES(2)
Commercial units (residual No. 6)[c]	223	0.04	0.3	ES(1)
Commercial units (residual No. 5)	88	0.01	0.09	ES(1)
Commercial units (residual No. 4)	86	0.02	0.2	ES(1)

[a] Uncontrolled unless otherwise specified.
[b] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.
[c] Particle size range (particulate collected with a cascade impactor): 20 percent (by weight) less than 0.21 micron, 80 percent less than 7.4 microns, mass mean particle size 1.2 microns.
[d] Not reported.

Table 9-4. EMISSION FACTORS FOR VANADIUM FROM SOLID WASTE INCINERATION

Source	Emission factor	Emission factor symbol [a]
Uncontrolled	0.0005 kg/10^3kg (0.001 lb/ton) of waste burned	EST (1)
After electrostatic precipitation	— [b]	EST (1)

[a] Defined in Table 1-1; numbers in parentheses indicate number of samples analyzed.

[b] Emissions below detection limit of analytical technique.